KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University)
(Established Under Section 3 of UGC Act 1956)
Coimbatore – 641 021.
(For the candidates admitted from 2018 onwards)

DEPARTMENT OF CHEMISTRY

SUBJECT NAME: PHYSICAL CHEMISTRY-III **SUBJECT CODE: 18CHP302**
SEMESTER: III **CLASS: II M. Sc CHEMISTRY**

Course outcome

To know about the concepts of activity and activity coefficients and determination of activity coefficient
- To familiarize the Partial molar properties and its determination
- To learn about the chemical potential and its determination
- To study the concept of thermodynamic probability
- To learn the Maxwell – Boltzmann, Fermi – Dirac and Bohr's Einstein statistics Comparison and applicationsTo know about the Partition functions

Course Objectives

1. To develop knowledge in the interpretation of various physical quantities involved in the thermodynamics.
2. To learn the fundamental process involved in thermodynamics and their applications.

UNIT – I

Themodynamics and Non-ideal systems: Chemical potential and the definition of fugacity. Determination of fugacity of gases by graphical method and from equations of state. Variation of fugacity with temperature. Fugacity and the standard states for non ideal gases.
Definition of activity. Activity coefficient. Temperature coefficient of activity. Standard states. Applications of activity concept to solutions. The rational and practical approaches. Measurement of activity of solvent from colligative properties. Determination of activity of solute.

UNIT – II

Third Law of Thermodynamics: Probability and third law. Need for third law. Nernst heat theorem and other forms stating third law. Thermodynamic quantities at absolute zero. Statistical meaning of third law and apparent exception.
Mathematical Introduction: Theories of permutation & combination, laws of probability. Distribution laws. Gaussian distribution.

UNIT – III

Classical Maxwell – Boltzmann Statistics: Maxwell distribution law for molecular velocities and molecular speeds in an ideal gas. Velocity and speed distribution functions. Experimental verification of Maxwell distribution law. Evaluation of average speed, root mean square speed and most probable speed from distribution law. Distribution function in terms of the kinetic energy of an ideal gas. The principle of equipartition of energy and the calculation of heat capacities of ideal gases. Limitations of the principle of equipartition of energy.

Quantum statistics: Maxwell-Boltzmann statistics. Thermodynamic probability. Thermodynamic probabilities of systems in equilibrium. Boltzmann expression for entropy. Stirling's approximation. State of maximum thermodynamics probability. Legrangian multipliers. Thermodynamic probabilities of systems involving energy levels. Maxwell-Boltzmann distribution law. Evaluation of alpha and beta in MB distribution law.

UNIT – IV

Partition function: Definition, justification of nomenclature, microcanonical and canonical ensembles. Molecular partition and canonical function. The relation between the total partition function of a molecule and the separate partition functions. Translational partition function, rotational partition function. Effect of molecular symmetry on rotational partition function. Ortho and para hydrogen. Vibrational partition function. Electronic partition function. Evaluation of thermodynamic properties E, H, S, A, G, C_v and C_p from monoatomic and diatomic ideal gas molecules partition functions. Thermodynamic properties of polyatomic ideal gases. Calculation of equilibrium constants of reaction involving ideal gases from partition functions.

UNIT – V

Heat capacities of solids: Einstein's and Debye's theories of heat capacities of solids. Bose-Einstein and Fermi-Dirac Statistics: Bose Einstein distribution law- Entropy of Bose Einstein gas. Planck distribution law of black body radiation. Fermi-Dirac distribution law. Entropy of a Fermi-Dirac gas. Heat capacities of the electron gas and the heat capacities of metals. Negative absolute temperature.

SUGGESTED READINGS:

Text Books:

1. Glasstone, S. (2002). *Thermodynamics for Chemists*. New York: Litton Edition Publishing.
2. Atkins, P., & De Paula, J. (2014). *Atkins Physical Chemistry* (X Edition). Oxford: Oxford University Press.
3. Kapoor, K. L. (2005). *Text Book Physical Chemistry Vol. V*. New Delhi: MacMillan India Ltd.

Reference Books:

1. Lavin, I. N. (2002). *Physical Chemistry* (V Edition). New Delhi: Tata-McGraw Hill Publishing Company.
2. Whittakar, A. G. (2001). *Physical Chemistry*. New Delhi: Mount & Heal Viva Books Pvt. Ltd.

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SUBJECT NAME: PHYSICAL CHEMISTRY-III **SUBJECT CODE: 18CHP302**

SEMESTER: III **CLASS: II M. Sc CHEMISTRY**

LECTURE PLAN

UNIT-I

Themodynamics and Non-ideal systems **Total no. of hours: 10**

S.No	Lecture Hour	Topics to be Covered	Support Materials
1.	1	Introduction - Themodynamics and Non-ideal systems- Chemical potential - Definition . Fugacity -Definition	R2-215 R2-251
2.	1	Determination of fugacity of gases by graphical method .	R2-251-252
3.	1	Determination of fugacity of gases from equations of state.	R2-253-254
4.	1	Variation of fugacity with temperature.	R2-261-262
5.	1	Definition of activity. Activity coefficient. Temperature coefficient of activity, Standard states. .	R1-582-583, R3-170
6.	1	Applications of activity concept to solutions, The rational and practical approaches.	R2-337-338
7.	1	Measurement of activity of solvent from colligative properties.	R2-356-357
8.	1	Determination of activity of solute.	R2-357-358
9.	1	Discussion of Question paper	

References:
1. Puri, Sharma & Pathania, 2003. Physical Chemistry, Vishal Publishing Co., Jalandar.

2.Glasstone, S. 2002.Thermodynamics for Chemists. Litton Edition Publishing, New York

3.Gurtu and Gurtu, 2000. Thermodynamics, Pragati pragasan publications, Chennai.

UNIT-II Third law of Thermodynamics

HOURS REQUIRED -09

S.No	Lecture Hour	Topics to be Covered	Support Materials
1.	1	Third Law of Thermodynamics- Introduction. Probability and third law.	
2.	1	Nernst heat theorem and other forms stating third law.	R1-586-587
3.	1	Thermodynamic quantities at absolute zero	R1-587
4.	1	Statistical meaning of third law.	R1-595
5.	1	Apparent exception-	
6.	1	Mathematical Introduction, Theories of permutation & combination	
7.	1	Laws of probability	
8.	1	Distribution laws, Gaussian distribution.	R3-836-838
9.	1	Discussion of question paper	

References:
1. Puri, Sharma & Pathania, 2003. Physical Chemistry, Vishal Publishing Co., Jalandar.

2. Gurtu and Gurtu, 2000. Thermodynamics, Pragati pragasan publications, Chennai

3. S.P.Gupta Statistical Methods

UNIT-III **Statistical Thermodynamics**

HOURS REQUIRED -12

S.No	Lecture Hour	Topics to be Covered	Support Materials
1.	1	Introduction to Statistical Thermodynamics- Classical Maxwell – Boltzmann statistics: Maxwell distribution law for molecular velocities in an ideal gas.	
2.	1	Maxwell distribution law for molecular speeds in an ideal gas.	R1-69
3.	1	Experimental verification of Maxwell distribution law	R3-1029-1030
4.	1	Evaluation of average speed, root mean square speed and most probable speed from distribution law.	
5.	1	Distribution function in terms of the kinetic energy of an ideal gas. The principle and limitations of equipartition of energy and the calculation of heat capacities of ideal gases.	R1-82
6.	1	Quantum statistics- Maxwell-Boltzmann statistics- Thermodynamic probability- Boltzmann expression for entropy.	R1-6302-631
7.	1	Stirling's approximation. State of maximum thermodynamics probability. Legrangian multipliers	R2-837
8.	1	Thermodynamic probabilities of systems involving energy levels.	
9.	1	Evaluation of alpha and beta in MB distribution law.	R1-634
10.	1	Recapitulation and Discussion of question paper	

References:

1. Puri, Sharma & Pathania, 2003. Physical Chemistry, Vishal Publishing Co., Jalandar.

2.Lavin, I.N 2002. Physical Chemistry. V Edition, Tata-Mc Graw Hill Publishing Company, New Delhi

3. . Mc.Quarrie Physical Chemistry

UNIT-IV **Partition function**

HOURS REQUIRED -10

S.No	Lecture Hour	Topics to be Covered	Support Materials
1.	1	Partition function- definition-justification of nomenclature- -	
2.	1	Microcanonical and canonical ensembles- Molecular partition and canonical function. .	
3.	1	The relation between the total partition function of a molecule and the separate partition functions.	
4.	1	Translational partition function	R1-637
5.	1	Rotational partition function Effect of molecular symmetry on rotational partition function.	R1-639
6.	1	Ortho and Para hydrogen-Vibrational partition function.	R1-640
7.	1	Electronic partition function. Evaluation of thermodynamic properties E,H,S,A,G,Cv and Cp from monoatomic ideal gas molecules partition functions.	R1-642, R1-648-649
8.	1	Thermodynamic properties of polyatomic ideal gases.	R1-645
9.	1	Calculation of equilibrium constants of reaction involving ideal gases from partition functions.	R1-652
10.	1	Discussion of important questions	

References:

1. Puri, Sharma & Pathania, 2003. Physical Chemistry, Vishal Publishing Co., Jalandar

UNIT-V **Heat capacity of solids**

HOURS REQUIRED -10

S.No	Lecture Hour	Topics to be Covered	Support Materials
1.	1	Heat capacities of solids-Introduction, Einstein's theories of heat capacities of solids.	R1-656
2.	1	Debye 's theories of heat capacities of solids.	R1-657
3.	1	Bose-Einstein and Fermi-Dirac Statistics-Bose Einstein distribution law Bose Einstein Condensation .	R1-632
4.	1	Entropy of Bose Einstein gas	R1-633
5.	1	Plank distribution law of black body radiation	
6.	1	Fermi-Dirac distribution law.	
7.	1	Entropy of Fermi-Dirac gas.	
8.	1	Heat capacities of the electron gas and the heat capacities of metals.	
9.	1	Negative absolute temperature.	
10	1	Discussion of Question paper	

References:

1. Puri, Sharma & Pathania, 2003. Physical Chemistry, Vishal Publishing Co., Jalandar

	Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answers
1	The study of the flow of heat or any other form of energy in to or out of a system undergoing physical or chemical change is called	thermochemistry	thermokinetics	thermodynamics	thermochemical studies.	thermodynamics
2	Thermodynamics is applicable to	microscopic systems only	macroscopic systems only	homogeneous systems only	heterogeneous systems only.	macroscopic systems only
3	Which is not true about thermodynamics	it ignores the internal structure of atoms and molecules	it involves the matter in bulk	it is concerned only with the initial and final states of the system	it is not applicable to macroscopic systems.	it is not applicable to macroscopic systems.
4	An system that can transfer neither matter nor energy to and from its surroundings is called	a closed system	an isolated system	an open system	a homogeneous system	an isolated system
5	A thermosflask is an example of	isolated system	closed system	open system	heterogeneous system	isolated system
6	A __________ is one which cannot transfer matter but transfer heat, work and radiations to and from its surroundings	an isolated system	an open system	a homogeneous system	a closed system	a closed system

7	A gas contained in a cylinder filled with a piston constitutes	an open system	a heterogeneous system	a closed system	an isolated system	a closed system
8	Which of the following is incorrect, for an ideal gas	PV= nRT	V= nRT/P	P=nRT/V	all are correct.	an open system
9	The heat capacity at constant pressure is related to heat capacity at constant volume by the relation	Cp-R =Cv	Cv-R =Cp	Cp-Cv =R	R-Cp =Cv	P=nRT/V
10	Which of the following relations is true	Cp>Cv	Cv>Cp	Cp=Cv	Cp=Cv=0.	Cp-R =Cv
11	An intensive property does not depend up on	nature of the substance	quantity of matter	external temperature	atmospheric pressure	Cp>Cv
12	Which of the following is not an intensive property	pressure	concentration	density	volume	volume
13	A property that depends up on the quantity of matter is called an extensive property. Which of the following is not an extensive	mass	volume	density	internal energy.	density
14	A system in which state variables have constant values throughout the system is called in a state	equilibrium	non- equilibrium	isothermal equilibrium	inequilibrium	equilibrium

	of					
15	In an adiabatic process ______ can flow in to or out of the system	no heat	heat	matter	no matter.	no heat
16	The mathematical relation for the first law of thermodynamics is	ΔE =q-w	ΔE = 0 for a cyclic process	ΔE =q for an isochoric process	all of these.	all of these.
17	For an adiabatic process according to first law of thermodynamics	ΔE = -w	ΔE = w	ΔE =q-w	Δ q = E-w	ΔE = -w
18	The enthalpy change, ΔH of a process is given by the relation	ΔH =ΔE +pΔv	ΔH =ΔE +ΔnRT	ΔH =ΔE +w	ΔH =ΔE -ΔnRT	ΔH =ΔE +ΔnRT
19	The amount of heat required to raise the temperature of one mole of the substance by 1 K is called	heat capacity	molar heat capacity	molar heat	molar capacity.	molar heat capacity
20	Heat capacity at constant pressure is the change in	internal energy with temperature at constant volume	internal energy with temperature at constant pressure	enthalpy with temperature at constant volume	enthalpy with temperature at constant pressure	enthalpy with temperature at constant pressure
21	Heat capacity at constant volume is the change in	internal energy with temperature at constant volume	internal energy with temperature at constant pressure	enthalpy with temperature at constant volume	enthalpy with temperature at constant pressure	internal energy with temperature at constant volume

22	The enthalpy change of a reaction is independent of	State of the reactants and products	nature of the reactants and products	initial and final enthalpy change of the reaction	different intermediate reaction	nature of the reactants and products
23	Which of the following is not correct ?	H=E+PV	H-E=PV	H-E-PV=0	H=E-PV	H=E-PV
24	The enthalpy of a system is defined by the relation	H=E+PV	H=E-PV	E=H+PV	PV+E-H	H=E+PV
25	For an endothermic reaction	ΔH is –ve	ΔH is +ve	ΔE is –ve	ΔH is zero	ΔH is +ve
26	A process which proceeds of its own accord, without any outside assistance is called	non-spontaneous process	spontaneous process	reversible process	ir reversible process	spontaneous process
27	The tendency of a process to occur naturally is called	momentum of the reaction	spontaneity of the reaction	equilibrium of the reaction	non-spontaneous of the reaction	spontaneity of the reaction
28	Which of the following is true about the criteria of spontaneity?	a spontaneous change is unindirectional	a spontaneous change to occur, time is no factor	once a system is in equilibrium,a spontaneous change is inevitable	all of these	all of these
29	A spontaneous change is accompanied by ________ of internal energy or enthalpy.	increase	decrease	neither increase nor decrease	decrease with increasing	decrease

30	Each substance in a given state has a tendency to escape from that state and this escaping tendency is called	spontaneity	Gibbs free energy	fugacity	activity	fugacity
31	A spontaneous reaction proceeds with a decrease in	entropy	enthalpy	free energy	internal energy .	free energy
32	The ratio f/f0 is called _________and is denoted by the symbol a.	activity	activity coefficient	chemical potential	fugacity.	activity
33	The ratio f/p is called _________ of a gas and is represented by the symbol υ.	activity	activity coefficient	chemical potential	fugacity.	activity coefficient
34	The variation of free energy with temperature at constant pressure is given by the relation	dGp = -SdTp	(dG/dT)p = -S	neither of these	free energy	free energy
35	The variation of free energy with pressure at constant temperature is given by the relation	(dG)T = -VdPT	dGp = -SdTp	(dG/dT)p = -S	(dG/dT) T = -S	(dG)T = -VdPT
36	For a spontaneous process	$\Delta G>0$	$\Delta G<0$	$\Delta G =0$	$\Delta S=0$	$\Delta G<0$
37	For an ideal gas , the fugacity is equal to pressure and ______	f/p =1	f/p=0	f/p varies	f/p> 1	f/p =1

38	For a real gas , the fugacity is not equal to pressure and the ratio _______	f/p =1	f/p=0	f/p varies	p/f =1	f/p varies
39	A process is in the equilibrium state when	ΔG>0	ΔG<0	ΔG =0	ΔS=0	ΔG =0
40	Which of the following equation is used to calculate the heats of reaction when ΔG at two temperatutes are given?	Gibbs Helmholtz equatioin	Clapeyron equation	Kirchoffs equation	Nernst equation	Gibbs Helmholtz equatioin
41	_____________ is applicable to macroscopic systems only.	thermochemistry	thermokinetics	thermodynamics	thermochemical studies.	thermodynamics
42	An example of isolated system	thermocouple	thermosflask	carnot engine	manometer	thermosflask
43	ideal gas can be represented as _____	PV =nRT	PR=mVT	PT=nVR	PT=VR	PV =nRT
44	ΔE =q-w for an isochoric process	first law of thermodynamics	second law of thermodynamics	zeroth's law	third law of thermodynamics	first law of thermodynamics
45	Which of the following is an extensive property ?	pressure	concentration	density	volume	volume
46	Which of the following is an intensive property ?	mass	volume	density	internal energy.	density

47	$\Delta E = q-w$ is the mathematical relation for the	first law of thermodynamics	second law of thermodynamics	third law of thermodynamics	zeroth's law	first law of thermodynamics
48	$\Delta E = -w$ represents ___________	adiabatic process	isothermal process	isobaric process	exoergic process	adiabatic process
49	ΔH is +ve for ____________	endothermic process	exothermic process	exoergic process	endoergic process	endothermic process
50	Spontaneous change is accompanied by decrease of ________	entropy	enthalpy	internal energy	free energy	internal energy
51	Raoults law is dilute ideal solution non ideal perfect gas to be quite satisfactory for a	dilute solution ideal non ideal solution			perfect gas	dilute solution
52	For an adiabatic process according to ---------------- of thermodynamics, $\Delta E = -w$	second law	first law	third law	zeroth law	first law
53	When two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other	First Law of Thermodynamics	Second Law of Thermodynamics	Mechanical equivalent of heat	Zeroth Law of Thermodynamics	Zeroth Law of Thermodynamics
54	Which of the following temperature scales doesn't have negative numbers	Celsius	Kelvin	Reaumur	Fahrenheit	Kelvin
55	Which of two temperature change are equivalent?	1 K = 1 F	1 F = 1 C	1 Re = 1 F	1 K = 1 C	1 K = 1 C

56	The partial molar free energy of an element A in solution is the same as its	Chemical potential	Activity	Fugacity	Activity coefficient	Chemical potential
57	The state of a system is identified by its	shape	size	properties	surroundings	properties
58	The solvent in a dilute solution follows	Henrys law	Daltons law	Raoults law	Charles law	Raoults law
59	The ratio of fugacity to fugacity at standard state is called the	Activity	Activity co-efficient	Fugacity coefficient	Chemical potential	Fugacity coefficient
60	The chemical potential of a pure substance is equal to the	specific Gibbs free energy	molar entropy	The Gibbs free energy	Molar Gibbs free energy	The Gibbs free energy

Partial molar property

A partial molar property is a thermodynamic quantity which indicates how an extensive property of a solution or mixture varies with changes in the molar composition of the mixture at constant temperature and pressure, or for constant values of the natural variables of the extensive property considered. Essentially it is the partial derivative with respect to the quantity (number of moles) of the component of interest. Every extensive property of a mixture has a corresponding partial molar property. Water and ethanol always have negative excess volumes when mixed, indicating the partial molar volume of each component is less when mixed than its molar volume when pure.

In general, the partial molar volume of a substance X in a mixture is the change in volume per mole of X added to the mixture.

The partial molar volumes of the components of a mixture vary with the composition of the mixture, because the environment of the molecules in the mixture changes with the composition. It is the changing molecular environment (and the consequent alteration of the interactions between molecules) that results in the thermodynamic properties of a mixture changing as its composition is altered

If *Z*, denotes a extensive property of a mixture, it depends on the pressure (*P*), temperature (*T*), and the amount of each component of the mixture (measured in moles, *n*). For a mixture with *m* components, this is expressed as

$$Z = Z(T, P, n_1, n_2, \cdots).$$

If temperature *T* and pressure *P* are held constant, $Z = Z(n_1, n_2, \cdots)$ is a homogeneous function of degree 1, since doubling the quantities of each component in the mixture will double *Z*. More generally, for any λ:

$$Z(\lambda n_1, \lambda n_2, \cdots) = \lambda Z(n_1, n_2, \cdots).$$

By Euler's first theorem for homogeneous functions, this implies

$$Z = \sum_{i=1}^{m} n_i \bar{Z}_i,$$

where $\bar{Z}_i$ is the partial molar *Z* of component *i* defined as:

$$\bar{Z}_i = \left(\frac{\partial Z}{\partial n_i}\right)_{T,P,n_{j\neq i}}.$$

By Euler's second theorem for homogeneous functions, $\bar{Z}_i$ is a homogeneous function of degree 0 which means that for any λ:

$$\bar{Z}_i(\lambda n_1, \lambda n_2, \cdots) = \bar{Z}_i(n_1, n_2, \cdots).$$

In particular, taking $\lambda = 1 / n_T$ where $n_T = n_1 + n_2 + \cdots$, one has

$$\bar{Z}_i(x_1, x_2, \cdots) = \bar{Z}_i(n_1, n_2, \cdots),$$

where $x_i = \dfrac{n_i}{n_T}$ is the concentration, or mole fraction of component *i*. Since the molar fractions satisfy the relation

$$\sum_{i=1}^{m} x_i = 1,$$

the x_i are not independent, and the partial molar property is a function of only $m - 1$ mole fractions:

$$\bar{Z}_i = \bar{Z}_i(x_1, x_2, \cdots, x_{m-1}).$$

The partial molar property is thus an intensive property - it does not depend on the size of the system.

Partial molar properties satisfy relations analogous to those of the extensive properties. For the internal energy *U*, enthalpy *H*, Helmholtz free energy *A*, and Gibbs free energy *G*, the following hold:

$$\bar{H}_i = \bar{U}_i + P\bar{V}_i,$$
$$\bar{A}_i = \bar{U}_i - T\bar{S}_i,$$
$$\bar{G}_i = \bar{H}_i - T\bar{S}_i,$$

where *P* is the pressure, *V* the volume, *T* the temperature, and *S* the entropy.

Differential form of the thermodynamic potentials

The thermodynamic potentials also satisfy

$$dU = TdS - PdV + \sum_i \mu_i dn_i,$$
$$dH = TdS + VdP + \sum_i \mu_i dn_i,$$
$$dA = -SdT - PdV + \sum_i \mu_i dn_i,$$
$$dG = -SdT + VdP + \sum_i \mu_i dn_i,$$

where μ_i is the chemical potential defined as (for constant n_j with $j \neq i$):

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P}.$$

The last partial derivative is the same as $\bar{G}_i$, the partial molar Gibbs free energy. This means that the partial molar Gibbs free energy and the chemical potential, one of the most important properties in thermodynamics and chemistry, are the same quantity. Under isobaric (constant *P*) and isothermal (constant *T*) conditions, the chemical potentials, $\mu_i(x_1, x_2, \cdots, x_m)$, yields every property of the mixture as they completely determine the Gibbs free energy.

Chemical potential :

Chemical potential, symbolized by μ, is a quantity first described Josiah Willard Gibbs.

Gibbs definition, any chemical element or combination of elements in given proportions may be considered a substance, whether capable or not of existing by itself as a homogeneous body. Chemical potential is also referred to as partial molar Gibbs energy. Chemical potential is measured in units of energy/particle or, equivalently, energy/mole.

Consider a thermodynamic system containing *n* constituent species. Its total internal energy *U* is postulated to be a function of the entropy *S*, the volume *V*, and the number of particles of each species $N_1, ..., N_n$

$$U = U(S, V, N_1, \ldots, N_n)$$

By referring to *U* as the *internal energy*, it is emphasized that the energy contributions resulting from the interactions between the system and external objects are excluded. For example, the gravitational potential energy of the system with the Earth are not included in *U*.

The chemical potential of the *i*-th species, μ_i is defined as the partial derivative

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}}$$

where the subscripts simply emphasize that the entropy, volume, and the other particle numbers are to be kept constant.

In real systems, it is usually difficult to hold the entropy fixed, since this involves good thermal insulation. It is therefore more convenient to define the Helmholtz energy *A*, which is a function of the temperature *T*, volume, and particle numbers:

$$A = A(T, V, N_1, \ldots, N_n)$$

In terms of the Helmholtz energy, the chemical potential is

$$\mu_i = \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j\neq i}}$$

The conditions at constant temperature and pressure. The chemical potential is the partial derivative of the Gibbs energy with respect to number of particles

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{j\neq i}}$$

The chemical potential can be written in terms of partial derivative of the enthalpy (conditions of constant entropy and pressure).

Here, the chemical potential has been defined as the energy per molecule. A variant of this definition is to define the chemical potential as the energy per mole.

The chemical potential is known in a certain state (e.g. for standard conditions), then it can be calculated in linear approximation for pressures and temperatures in the vicinity of thisstate:

$\mu(T)=\mu(T_0)+\alpha(T-T_0)$ and

$\mu(p)=\mu(p_0)+\beta(p-p_0)$

Here $\alpha = \left(\frac{\partial \mu}{\partial T}\right)_{p,n}$ is the temperature coefficient and

$\beta = \left(\frac{\partial \mu}{\partial p}\right)_{T,n}$ is the pressure coefficient.

With the Maxwell relations

$$\left(\frac{\partial \mu}{\partial T}\right)_{p,n} = -\left(\frac{\partial S}{\partial n}\right)_{T,p}$$

and

$$\left(\frac{\partial \mu}{\partial p}\right)_{T,n} = \left(\frac{\partial V}{\partial n}\right)_{T,p}$$

It follows that the temperature coefficient is equal to the negative molar entropy and the pressure coefficient is equal to the molar volume.

Fugacity :

Fugacity is the effective pressure for a non-ideal gas. The pressures of an ideal gas and a real gas are equivalent when the chemical potential is the same. The equation that relates the non-ideal to the ideal gas pressure is:

$\Phi = f / P$

In this equation, f represents fugacity, P is the pressure for an ideal gas, and Φ is the fugacity coefficient. For an ideal gas, the fugacity coefficient is 1.

Fugacity (*f*) is a chemical quantity with units of pressure.

Determination of Fugacity of gases by graphical method and from equations of state.

The Gibbs free energy depends on pressure as well as on temperature. The pressure dependence of the Gibbs free energy in a closed system is given by the combined first and second laws and the definition of Gibbs free energy as,

$dG = -SdT + Vdp \quad \longrightarrow 1$

If we hold temperature constant and vary only the pressure. Equation 1 for integration from pressure p_1 to p_2 as follows:

$$dG = Vdp \longrightarrow 2$$

Then

$$G(p_2) - G(p_1) = \int_{p_1}^{p_2} Vdp \longrightarrow 3$$

or

$$G(p_2) = G(p_1) + \int_{p_1}^{p_2} Vdp \; . \longrightarrow 4$$

Equation 4 is general and applies to all isotropic substance: solids, liquids, ideal gases, and real gases.

Solids and Liquids

The solids and liquids are not very compressible so, to a first approximation, regard the volume in Equation 4 as constant (as long as the range of pressure is not too large). Then the V in Equation 4 comes out of the integral and integrate easily to get,

$$G(p_2) = G(p_1) + V(p_2 - p_1) \longrightarrow 5$$

However, that solids and liquids are slightly compressible and define the isothermal compressibility as

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \longrightarrow 6$$

The second level of approximation is to regard κ as approximately constant. (κ is not constant, but the variation with pressure is so small it can be ignored) With κ regarded as constant rearrange Equation 6 and integrate it to find an expression for V as a function of p (which can then be substituted into Equation 4 and integrated.) Rearrangement of Equation 6,

$$\frac{dV}{V} = -\kappa\, dp \qquad \longrightarrow 7$$

Integrate from p_1 to p_2 (and volume goes from V_1 to V_2) to get,

$$\ln \frac{V_2}{V_1} = -\kappa\, (p_2 - p_1) \qquad \longrightarrow 8$$

Take the antilog of both sides,

$$V_2 = V_1 e^{-\kappa (p_2 - p_1)} \qquad \longrightarrow 9$$

In Equation 9 let p_1 be a constant and let p_2 range over the pressures. There is no reason why we have to keep the subscript "2" on p_2 so change p_2 to just p. This gives us V as a function of p,

$$V = V_1 e^{-\kappa (p - p_1)} = V_1 e^{\kappa p_1} e^{-\kappa p} \qquad \longrightarrow 10$$

Equation 10 the constant parts have been separated from the variable part to make it easy to integrate. When this expression for V is plugged into Equation 4 only the $e^{-\kappa p}$ need stay inside the integral.

Ideal Gases

Equation 4 is also valid for gases, only here we put in the value of V for an ideal gas.

$$V = \frac{nRT}{p} \longrightarrow 11$$

With this substitution Equation 4 becomes,

$$G(p_2) = G(p_1) + \int_{p_1}^{p_2} \frac{nRT}{p} dp \longrightarrow 12$$

After integration Equation 12 becomes.

$$G(p_2) = G(p_1) + nRT \ln \frac{p_2}{p_1} \longrightarrow 13$$

Let p_2 range over the pressures p, let p_1 be some standard state pressure and call it p^o, and finally we divide through by the number of moles of gas, n. With these changes equation 13 is written,

$$\frac{G(p)}{n} = \frac{G(p^o)}{n} + RT \ln \frac{p}{p^o} \longrightarrow 14$$

The quantity G/n , represents the Gibbs free energy per mole of substance. This quantity is called the chemical potential and it is given the symbol, μ .

$$\mu = \mu^o + RT \ln \frac{p}{p^o} \longrightarrow 15$$

Replaced $G(p^o)/n$, the molar Gibbs free energy at the standard state pressure, with its chemical potential symbol, μ^o. The standard state pressure equal to one atmosphere.

$$\mu = \mu^o + RT \ln p \longrightarrow 16$$

$p^o = 1$ atm dividing the p in the ln p.

Nonideal Gases

Equation 15 was derived assuming the gas is ideal. It does not apply to real gases or approximations to a real gas, like the van der Waals equation of state. Divide Equation 4 by the number of moles, *n*, let p_1 equal the standard state pressure, p^o and *V/n* is the molar volume to get,

$$\mu = \mu^o + \int_{p^o}^{p} \overline{V}(p')dp' \longrightarrow 17$$

Let p_2 range over the pressures *p*, variable of integration from *p* to *p'*.) Equation 17 ,the equilibrium constant expression. Equation 15 by writing the chemical potential as,

$$\mu = \mu^o + RT\ln\frac{f(p)}{p^o} \longrightarrow 18$$

This equation defines a quantity *f* (*p*) called the fugacity. The fugacity has units of pressure and it is a function of pressure. It contains the non ideality of the gas. For an ideal gas the fugacity is the same as the pressure. Since all real gases become ideal in the limit as pressure goes to zero,

$$\lim_{p\to o} f(p) = p \longrightarrow 19$$

From the equation of state for a gas, Equation 2 and divide it by the number of moles, *n*,

$$d\frac{G}{n} = \frac{V}{n}dp \longrightarrow 20$$

or

$$d\mu = \overline{V}dp \longrightarrow 21$$

Another expression for $d\mu$ by taking the differential of Equation 18 (R, T, p^o , and μ^o are constants.)

$$d\mu = RTd\ln f \longrightarrow 22$$

$d\mu$ in Equations 21 and 22 must be the same, so equal to each other

$$RTd\ln f = \overline{V}dp \longrightarrow 23$$

Rearrange this to get,

$$d\ln f = \frac{\overline{V}}{RT}dp \longrightarrow 24$$

Integrate this equation directly, Add and subtract $\frac{dp}{p}$ to the right hand side of Equation 24,

$$d\ln f = \frac{\overline{V}}{RT}dp - \frac{dp}{p} + \frac{dp}{p} \longrightarrow 25$$

Regroup the terms in Equation 25,

$$d\ln f = \left(\frac{\overline{V}}{RT} - \frac{1}{p}\right)dp + \frac{dp}{p} \longrightarrow 26$$

$$\ln f - \ln f_o = \int_{p_o}^{p}\left(\frac{\overline{V}(p')}{RT} - \frac{1}{p'}\right)dp' + \ln p - \ln p_o \longrightarrow 27$$

where f_o is the fugacity at p_o. Move the $\ln f_o$ to the right hand side,

$$\ln f = \int_{p_o}^{p}\left(\frac{\overline{V}(p')}{RT} - \frac{1}{p'}\right)dp' + \ln p + \left(\ln f_o - \ln p_o\right) \longrightarrow 28$$

The limit where p_o goes to zero. f_o goes to p_o as $p_o \rightarrow 0$ so the last two terms in parentheses on the right cancel each other in this limit. Equation 28 becomes,

$$\ln f = \int_0^p \left(\frac{\overline{V}(p')}{RT} - \frac{1}{p'} \right) dp' + \ln p \longrightarrow 29$$

Equation 29 will calculate the fugacity, but to take the antilog of both sides to get,

$$f = pe^{\int_0^p \left(\frac{\overline{V}(p')}{RT} - \frac{1}{p'} \right) dp'} = pe^{\int_0^p \frac{1}{p'}(Z-1)\, dp'} \longrightarrow 30$$

From Equation 29, $Z = \frac{p'\overline{V}}{RT}$, is the so-called compressibility factor. Equation 29 if the gas is ideal *f* = *p*. It requires an equation of state or experimental data to calculate a fugacity from either Equation 30 or Equation 29. From the right-hand side of Equation 30

$$\frac{p\overline{V}}{RT} = 1 + B'p + C'p^2 + \cdots \longrightarrow 31$$

would be the best method for calculating fugacity.

Variation of fugacity with temperature :

For a given temperature T, the fugacity *f* satisfies the following differential relation:

$$d \ln \frac{f}{f_0} = \frac{dG}{RT} = \frac{\bar{V} dP}{RT}$$

where G is the Gibbs free energy, R is the gas constant, v is the fluid's molar volume, and f_0 is a reference fugacity which is generally taken as 1 bar. For an ideal gas, when *f* = *P*, this equation reduces to the ideal gas law.

$$\mu_i = \mu_i + RT \ln f_i \longrightarrow 1$$

Dividing the equation throughout by T

$$\mu_i / T = \mu_i / T + R \ln f_i$$

$R \ln f_i = \mu_i / T - \mu_i / T \rightarrow 2$

We know that

$[\partial(\mu_i / T) / \partial T)]_{P,N} = -H_i / T^2 \rightarrow 3$

Differentiating equation 2 with respect to T at constant P and N

$R.\partial (\ln f_i) / \partial T = \partial(\mu_i / T) / \partial T - \partial(\mu_i / T) / \partial T$

$\partial (\ln f_i) / \partial T = H_i - H_i / RT^2$.

Activity

Activity is a measure of the effective concentration of a species under non-ideal (e.g., concentrated) conditions. This determines the real chemical potential for a real solution rather than an ideal one.

Activities and concentrations can both be used to calculate equilibrium constants and reaction rates. However, most of the time we use concentration even though activity is also a measure of composition, similar to concentration. It is satisfactory to use concentration for diluted solutions, but when you are dealing with more concentrated solutions, the difference in the observed concentration and the calculated concentration in equilibrium increases. This is the reason that the activity was initially created.

$a = e\mu - \mu o / RT$

where a=Activity, μ is chemical potential (dependent on standard state) which is Gibbs Energy per mole, $\mu 0$ is the standard chemical potential, R is the gas constant, T is the absolute Temperature.

The activity of a species *i*, denoted a_i, is defined as:

$$a_i = \exp\left(\frac{\mu_i - \mu_i^\ominus}{RT}\right)$$

where μ_i is the chemical potential of the species under the conditions of interest, $\mu^\ominus{}_i$ is the chemical potential of that species in the chosen standard state, R is the gas constant and T is the thermodynamic temperature. This definition can also be written in terms of the chemical potential:

$$\mu_i = \mu_i^\ominus + RT\ln a_i$$

The activity will depend on any factor that alters the chemical potential. These include temperature, pressure, chemical environment etc. The activity also depends on the choice of standard state, as it describes the difference between an actual chemical potential and a standard chemical potential. In principle, the choice of standard state is arbitrary, although there are certain conventional standard states which are usually used .

Activity coefficient

The activity coefficient γ, which is also a dimensionless quantity, relates the activity to a measured amount fraction x_i, molality m_i or amount concentration c_i:

$$a_i = \gamma_{x,i}x_i$$
$$a_i = \gamma_{m,i}m_i/m^\ominus$$
$$a_i = \gamma_{c,i}c_i/c^\ominus$$

The division by the standard molality $m^\ominus$ or the standard amount concentration $c^\ominus$ is necessary to ensure that both the activity and the activity coefficient are dimensionless, as is conventional.

When the activity coefficient is close to one, the substance shows almost ideal behaviour according to Henry's law. In these cases, the activity can be substituted with the appropriate dimensionless measure of composition x_i, $m_i/m^\ominus$ or $c_i/c^\ominus$. It is also possible to define an activity coefficient in terms of Raoult's law: the symbol *f* for this activity coefficient, although this should not be confused with fugacity.

$a_i = f_i x_i$. Solution can also become too diluted when necessary.

Standard states

Gases

A real gas and an ideal gas is dependent only on the pressure and the temperature, not on the presence of any other gases. At a given temperature, the "effective" pressure of a gas *i* is given by its fugacity f_i: this may be higher or lower than its mechanical pressure. Fugacities have the dimension of pressure, so the dimensionless activity is given by:

$$a_i = \frac{f_i}{p^\ominus} = \phi_i x_i \frac{p}{p^\ominus}$$

where φ_i is the dimensionless fugacity coefficient of the species, x_i is its fraction in the gaseous mixture ($x = 1$ for a pure gas) and p is the total pressure.

Mixtures in general

The most convenient way of expressing the composition of a generic mixture is by using the amount fractions x of the different components, where

$$x_i = \frac{n_i}{n}$$
$$\sum_i x_i = 1$$

The standard state of each component in the mixture is taken to be the pure substance, i.e. the pure substance has an activity of one. When activity coefficients are used, they are usually defined in terms of Raoult's law,

$$a_i = f_i x_i$$

where f_i is the Raoult's law activity coefficient: an activity coefficient of one indicates ideal behaviour according to Raoult's law.

Dilute solutions (non-ionic)

A solute in dilute solution usually follows Henry's law rather than Raoult's law, and it is more usual to express the composition of the solution in terms of the amount concentration c (in mol/L) or the molality m (in mol/kg) of the solute rather than in amount fractions.

The activity of the solute is given by:

$$a_{c,i} = \gamma_{c,i}\,\frac{c_i}{c^{\ominus}}$$

$$a_{m,i} = \gamma_{m,i}\,\frac{m_i}{m^{\ominus}}$$

Ionic solutions

When the solute undergoes ionic dissociation in solution (a salt e.g.), the system becomes non-ideal and the dissociation process is considered. The activities for the cations and anions separately (a_+ and $a_–$).

In a liquid solution the activity coefficient of a given ion (e.g. Ca^{2+}) isn't measurable because it is experimentally impossible to independently measure the electrochemical potential of an ion in solution. (We cannot add cations without putting in anions at the same time). Therefore ,

mean ionic activity $a_{\pm}^{v} = a_{+}^{v+}a_{–}^{v–}$
mean ionic molality $m_{\pm}^{v} = m_{+}^{v+}m_{–}^{v–}$
mean ionic activity coefficient $\gamma_{\pm}^{v} = \gamma_{+}^{v+}\gamma_{–}^{v–}$

where $v = v_+ + v_–$ represent the stoichiometric coefficients involved in the ionic dissociation process

Even though γ_+ and γ_- cannot be determined separately, $\gamma_\pm$ is a measureable quantity that can also be predicted for sufficiently dilute systems using Debye–Hückel theory. For the activity of a strong ionic solute (complete dissociation):

$$a_2 = a_\pm^{v} = \gamma_\pm^{v} m_\pm^{v}$$

The activity of a species is to measure its partial vapor pressure in equilibrium with a number of solutions of different strength. For some solutes this is not practical, sucrose or salt (NaCl) do not have a measurable vapor pressure at ordinary temperatures. However, in such cases it is possible to measure the vapor pressure of the *solvent* instead. Using the Gibbs–Duhem relation it is possible to translate the change in solvent vapor pressures with concentration into activities for the solute.

Another way to determine the activity of a species is through the manipulation of colligative properties, specifically freezing point depression. Using freezing point depression techniques, it is possible to calculate the activity of a weak acid from the relation,

$$m' = m(1 + a)$$

where m' is the total molal equilibrium concentration of solute determined by any colligative property measurement(in this case ΔT_{fus}, m is the nominal molality obtained from titration and a is the activity of the species.

There are also electrochemical methods that allow the determination of activity and its coefficient.

The value of the mean ionic activity coefficient $\gamma_\pm$ of ions in solution can also be estimated with the Debye–Hückel equation, the Davies equation or the Pitzer equations.

Chemical activities should be used to define chemical potentials, where the chemical potential depends on the temperature T, pressure p and the activity a_i according to the formula:

$$\mu_i = \mu_i^\ominus + RT \ln a_i$$

where *R* is the gas constant and $\mu_i^\ominus$ is the value of μ_i under standard conditions.

Formulae involving activities can be simplified by considering that:

For a chemical solution: the solvent has an activity of unity

At a low concentration, the activity of a solute can be approximated to the ratio of its concentration over the standard concentration:

$$a_i = \frac{c_i}{c^\ominus}$$

Therefore, it is approximately equal to its concentration.

For a mix of gas at low pressure, the activity is equal to the ratio of the partial pressure of the gas over the standard pressure:

$$a_i = \frac{p_i}{p^\ominus}$$

Therefore, it is equal to the partial pressure in bars (compared to a standard pressure of 1 bar).

For a solid body, a uniform, single species solid at one bar has an activity of unity. The same thing holds for a pure liquid.

The definition based on Raoult's law, let the solute concentration x_1 go to zero, the vapor pressure of the solvent p will go to p^*. Thus its activity $a = p/p^*$ will go to unity. This means that if during a reaction in dilute solution more solvent is generated (the reaction produces water e.g.) and typically set its activity to unity.

Solid and liquid activities do not depend very strongly on pressure because their molar volumes are typically small. Changes can also come as a result of too much dilution of solution.

Raoult's Law

At boiling and higher temperatures the sum of the individual component partial pressures becomes equal to the overall pressure, which can symbolized as P_{tot}.

Under such conditions, Dalton's Law would be in effect as follows:

$P_{tot} = P_1 + P_2 + ...$

Then for each component in the vapor phase:

$y_1 = P_1/P_{tot}$, $y_2 = P_2/P_{tot}$, ... etc.

where P_1 = partial pressure of component 1, P_2 = partial pressure of component 2, etc.

Raoult's Law is approximately valid for mixtures of components between which there is very little interaction other than the effect of dilution by the other components. Examples of such mixtures includes mixtures of alkanes, which are non-polar, relatively inert compounds in many ways, so there is little attraction or repulsion between the molecules. Raoult's Law states that for components 1, 2, etc. in a mixture:

$P_1 = x_1 P^0{}_1$, $P_2 = x_2 P^0{}_2$, etc.

where $P^0{}_1$, $P^0{}_2$, etc. are the vapor pressures of components 1, 2, etc. when they are pure, and x_1, x_2, etc. are mole fractions of the corresponding component in the liquid.

The vapor pressures of liquids are very dependent on temperature. Thus the P^0pure vapor pressures for each component are a function of temperature (T): For example, commonly for a pure liquid component, the Clausius-Clapeyron equation (not shown here) may be used to approximate how the vapor pressure varies as a function of temperature. This makes each of the partial pressures dependent on temperature also regardless of whether Raoult's Law applies or not. When Raoult's Law is valid these expressions become:

$P_1(T) = x_1 P^0{}_1(T)$, $P_2(T) = x_2 P^0{}_2(T)$, etc.

At boiling temperatures if Raoult's Law applies, the total pressure becomes:

$P_{tot} = x_1 P^0{}_1(T) + x_2 P^0{}_2(T) + ...$

At a given P_{tot} such as 1 atm and a given liquid composition, T can be solved for to give the liquid mixture's boiling point or bubble point, although the solution for T may not be mathematically analytical (may require a numerical solution or approximation). For a binary mixture at a given P_{tot}, bubble point T can become a function of x_1 (or x_2).

At boiling temperatures if Raoult's Law applies, expressions for vapor mole fractions as a function of liquid mole fractions and temperature:

$y_1 = x_1 P^0{}_1(T)/P_{tot}$,

$y_2 = x_2 P^0{}_2(T)/P_{tot}$, ... etc.

Once the bubble point T's as a function of liquid composition in terms of mole fractions have been determined, these values can be plugged into the above equations to obtain corresponding vapor composition in terms of mole fractions. The complete range of liquid mole fractions and their corresponding temperatures, obtains a temperature (T) function of vapor composition mole fractions. This function . In the case of a binary mixture: $x_2 = 1 - x_1$ and the above equations can be expressed as:

$y_1 = x_1 P^0{}_1(T)/P_{tot}$ and

$y_2 = (1 - x_1) P^0{}_2(T)/P_{tot}$

For many kinds of mixtures, particularly where there is interaction between components beyond simply the effects of dilution, Raoult's Law does not work well for determining the shapes of the curves in the boiling point or VLE diagrams. Even in such mixtures, there are usually still differences in the vapor and liquid equilibrium concentrations at most points, and distillation is often still useful for separating components at least partially.

Applications of activity concept to solutions:

Raoult's Law

Raoult's law states that the vapor pressure of a solvent above a solution is *equal* to the vapor pressure of the pure solvent at the same temperature *scaled* by the mole fraction of the solvent present:

$P_{solution}=X_{solvent}P^{o}_{solvent}$

Henry's Law

Henry's law is one of the gas laws formulated by William Henry in 1803. It states: "At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid." An equivalent way of stating the law is that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid.

To explain this law, Henry derived the equation:

$C=kPgas$

Where C is the solubility of a gas at a fixed temperature in a particular solvent (in units of M or mL gas/L) , k is Henry's law constant (often in units of M/atm), Pgas is the partial pressure of the gas (often in units of Atm).

The rational and practical approaches :
If the concentration of solution is expressed in terms of solution is expressed in terms of mole fraction it is referred to as the rational system and if molality or molarity is used for expressing concentration it is called practical system.

Measurement of activity of solvent from colligative properties:

Colligative properties are those properties which depend up on the number of particles and not the nature of solute.

These are properties of solutions in the dilute limit, where there is a solvent "A" and a solute "B" where nA >> nB. These properties are a direct result of $\mu^{mix}_{A}(\ell,T,p) < \mu^{pure}_{A}(\ell,T,p)$ Using two measures of concentration:

a. Mole Fraction: xB = nB/(nA+nB) ~ nB/nA

b. Molalility: mB = (moles solute)/(kg solvent) = nB/(nAMA) Where MA is the mass in kg of one mole of solvent.

There are four Colligative Properties:

1. Lowering of Vapor pressure
2. Elevation of Boiling point
3. Depression of Freezing point
4. Osmotic pressure

Rational activity of solvent from lowering of Vapor pressure: This is Raoult's Law.

Consider a solution which is in equilibrium with its vapour

Then, $\mu(\ell) = \mu(g)$ _________>1

$\mu(\ell) = \mu^\circ(\ell) + RT\ln a$ _________>2

Substitute second equation in first equation

$\mu(g) = \mu^\circ(\ell) + RT\ln a$ _________>3

Assuming ideal behavior for vapour

$\mu(g) = \mu^\circ(g) + RT\ln P$ _________>4

Substitute 4th equation in 3rd equation

$\mu^\circ(g) + RT\ln P = \mu^\circ(\ell) + RT\ln a$ _________>5

For pure liquid

$\mu^\circ(\ell) = \mu^\circ(g) + RT\ln P^\circ$ _________>6

Subtracting 6th from 5th equation

$RT\ln a = RT\ln P/P^\circ$

$A = P/P^\circ$

Where a= activity, P=Partial pressure, P◦ = Vapour pressure of pure solvent

Rational activity of solvent from Elevation of Boiling point

$\mu(\ell) = \mu(g) \rightarrow 1$

$\mu(\ell) = \mu^\circ(\ell) + RT\ln a \rightarrow 2$

$\mu(g) = \mu^\circ(\ell) + RT\ln a \rightarrow 3$

$\ln a = \mu(g) - \mu^\circ(\ell)/RT = \Delta\bar{G}vap/RT \rightarrow 4$

$d/dT \ln a = \frac{1}{R}\frac{d}{dT}(\Delta Gvap/RT) \rightarrow 5$

$d/dT \ln a = -\bar{H}vap/RT^2$

$\int d\ln a = -\bar{H}^\circ vap/RT\int_{T^\circ}^{T} dT/T^2 \rightarrow 6$

$\ln a = Hvap/R\,[1/T - 1/T^\circ]$

T is the Boiling point of solution

T° Boiling point of pure solvent.

Rational activity of solvent from Depression of Freezing point

$\mu(\ell) = \mu^\circ(s) \rightarrow 1$

$\mu(\ell) = \mu^\circ(\ell) + RT\ln a \rightarrow 2$

Substitute second equation in first equation

$\mu^\circ(s) = \mu^\circ(\ell) + RT\ln a$

$\ln a = \mu^\circ(s) - \mu^\circ(\ell) \rightarrow 3$

$\underline{\qquad\qquad\qquad}$

RT

$$\frac{[\mu^\circ(\ell) - \mu^\circ(s)]}{[RT]} = -\Delta G^\circ fus/RT \rightarrow 4$$

$$d\ln a/dT = \frac{-1}{R}\,\frac{d}{dT}\,\frac{(\Delta G^\circ fus)}{T} = \Delta H_{fus}/RT^2 \rightarrow 5$$

$$\int d\ln a = -H_{fus}/R\int_{T^\circ}^{T} dT/T^2 \rightarrow 6$$

$\ln a = -\Delta H_{fus}/R\,[1/T - 1/T^\circ]$

Thus knowing the freezing point ‘a’ can be calculated.

Osmotic Pressure

Osmosis is the diffusion of a fluid through a semipermeable membrane. When a semipermeable membrane (animal bladders, skins of fruits and vegetables) separates a solution from a solvent, then only solvent molecules are able to pass through the membrane. The osmotic pressure of a solution is the pressure difference needed to stop the flow of solvent across a semipermeable membrane. The osmotic pressure of a solution is proportional to the molar concentration of the solute particles in solution.

$\Pi = nRT/V = MMRT$

Where Π is the osmotic pressure, R is the ideal gas constant (0.0821 L atm / mol K),T is the temperature in Kelvin, n is the number of moles of solute present, V is the volume of the solution (n /V is then the molar concentration of the solute), and MM is the molar mass of the solute.

	Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answers
1	The third law of thermodynamics states that in the limit T→0	G=0	H=0	Cv=0	S=0	S=0
2	In the limit T→0 for a crystal	ST =Cp/2	ST=Cp/3	ST=Cp/4	ST=Cp	ST=Cp/3
3	Entropies calculated using the third law are called--------	thermal entropies	statistical entropies	residual entropies	absolute entropies	thermal entropies
4	The entropies of substance such as CO,NO,H_2O are not zero at 0 k as the third law formulates but are finite these entropies are called	thermal entropies	statistical entropies	residual entropies	absolute entropies	residual entropies
5	---------is the ratio of the number of cases favourable to the occurrence of an event to the total number of equally probable cases	mathematical probability	thermodynamic probability	statistical thermodynamics	classical mechanics	mathematical probability
6	---------is the number of microstates correcting to a given macrostate dealing with the distribution of molecules among on extremely large number of energy levels	.mathematical probability	thermodynamic probability	statistical thermodynamics	classical mechanics	thermodynamic probability

7	The boltzman entropy equation is probably the most famous equation in---------------	statistical thermodynamics	mathematical probability	thermodynamic probability	classical mechanics	statistical thermodynamics
8	The entropies of real gas behaves ideally at-----pressure	high	low	very high	very low	low
9	The absolute entropy zero of HCl at 25°C has the extrapolation from 0 to 15 K (using the Debye T^3 law is _____________	1.3 JK^{-1} mol^{-1}	29.5 JK^{-1} mol^{-1}	12.1 JK^{-1} mol^{-1}	10.1 JK^{-1} mol^{-1}	1.3 JK^{-1} mol^{-1}
10	10. The absolute entropy zero of HCl at 25ºc ∫Cp d ln T from 188.07 to 298.15K is ____________	13 .5 JK^{-1} mol^{-1}	29.5 JK^{-1} mol^{-1}	12.1 JK^{-1} mol^{-1}	10.1 JK^{-1} mol^{-1}	13 .5 JK^{-1} mol^{-1}
11	ΔS_{mix} of ortho hydrogen and para hydrogen is found to be _______ JK^{-1} mol^{-1} in the vicinity of 0 k.	0.37	16.22	17.1	19.66	0.37
12	The calorimetric value of entropy for CO is _________ JK^{-1} mol^{-1} .	155.5	4.6	160.1	171.2.	155.5
13	Every substance has a finite entropy which may become zero at absolute zero of temperature is __________ 0f thermodynamics.	second law	third law	first law	zeroth law	third law
14	The S_{mix} of CO is found to __________ JK^{-1} mol^{-1} .	5.76	6.72	1.25	3.56	5.76

15	The residual entropy of hydrogen is _______ JK^{-1} mol^{-1} .	6.23	4.25	5.62	3.15.	6.23
16	The entropy of S_{mixed} crystal is given by _________-	$-Nk\ [\ x_a ln\ x_a + x_b ln\ x_b\ ]$	$Nk\ [\ x_a ln\ x_a - x_b ln\ x_b\ ]$	$-Nk\ [\ -x_a ln\ x_a + x_b ln\ x_b\ ]$	$-Nk\ [-\ x_a ln\ x_a - x_b ln\ x_b\ ]$	$-Nk\ [\ x_a ln\ x_a + x_b ln\ x_b\ ]$
17	The residual entropy of hydrogen is due to the existence of __________ form of hydrogen in different quantum state.	ortho	para	both	combination	ortho
18	The calorimetric value of entropy in N_2O is _______ JK^{-1} mol^{-1}	198	202.1	227.2	232.1	198
19	The spectroscopic value of entropy in NO is _______ JK^{-1} mol^{-1}	172.8	182.8	198	202.7	182.8
20	The calorimetric value for NO is _______ JK^{-1} mol^{-1}	179.8	182.8	198	d)202.7	179.8
21	__________ is an arrangement that can be made by taking some or all of a number of given things.	permutations	combination	probability	independent events	permutations
22	___________ is a group (or selection) that can be made by taking some or all of a number of given things at a time.	permutations	combination	probability	independent events	combination

23	The total number of possible outcomes in any trial is known as ______	exhaustive events	favourable events	mutually exclusive events	independent events	exhaustive events
24	Events are said to be incompatible if the happening of any one of them rules out the happening of all others is called _________	exhaustive events	favourable events	mutually exclusive events	independent events	mutually exclusive events
25	The binomial distribution discovered by a swiss mathematician _________	James Bernoulli	Simeon Devis Poisson	De-Movire	Lapalace.	James Bernoulli
26	Poisson distribution was discovered by the French mathematician _________	James Bernoulli	Simeon Devis Poisson	De-Movire	Lapalace.	Simeon Devis Poisson
27	A continous random variable x assuming non-negative values is said to have an ___________ distributioin.	Binomial	Poisson	Geometric	Exponential	Exponential
28	_________ distribution is called continous probability distribution.	Binomial	Poisson	Geometric	Normal	Normal
29	_____________ distribution is called discrete probability distribution.	Normal	Exponential	Gaussian	Binomial	Binomial
30	__________ distribution is called continous probability distribution	Binomial	Poisson	Geometric	Exponential	Exponential
31	The entropy is measured in	cal K^{-1} mol^{-1}	J K^{-1} mol^{-1}	entropy unit	entropy	J K^{-1} mol^{-1}

32	The standard entropy, S$^{\circ}$, of a substance is	its entropy at 0˚c and 1 atm pressure	) its entropy at 0 K and 1 atm pressure	its entropy at 25˚c and 1 atm pressure	its entropy at 25 K and 1 atm pressure	its entropy at 25˚c and 1 atm pressure
33	The thermal entropies are somewhat smaller than the statistical entropies, the deviation ranging from ___________ J K^{-1} mol^{-1}	3.1-4.8	6.2-7	above 7	7.5 –8.2	3.1-4.8
34	The entropies of substance such as H$_2$, D$_2$ are not zero at 0 K as the third law formulates but are finite these entropies are called __________	thermal entropies	residual entropies	statistical entropies	absolute entropies	residual entropies
35	The entropy of a pure crystal is zero at absolute zero.This is statement of	first law of thermodynamics	second law of thermodynamics	third law of thermodynamics	zeroth law of thermodynamics	third law of thermodynamics
36	Which is the correct unit for entropy ?	kJ mol	J K^{-1} mol^{-1}	J K^{-1}mol	kJ mol.	J K^{-1} mol^{-1}
37	The probability of a sure event is	1	2	three	unlimited	1
38	The probability of an impossible event is	1	2	three	0	0
39	The probability of having at least one tail in 4 throws with a coin is	15/16	three	2	1	15/16

40	A dice is thrown once, then the probability of getting a number greater than three is	one/two	two/three	6	0	one/two
41	In the limit T→0 ; S= 0 which represents ______	first law of thermodynamics	second law of thermodynamics	third law of thermodynamics	zeroth's law	third law of thermodynamics
42	Entropies calculated using the _______ are called residual entropies.	first law of thermodynamics	second law of thermodynamics	third law of thermodynamics	zeroth's law	third law of thermodynamics
43	Which entropy equation is probably the most famous equation in statistical thermodynamics	Gibbs Helmholtz	Kirchoff's	Boltzmann	Clapeyron	Boltzmann
44	A real gas behaves ideally at low pressure	enthalpy	entropy	internal energy	heat capacity	entropy
45	The ortho hydrogen and para hydrogen is found to be 18.37 JK^{-1} mol^{-1} in the vicinity of 0 k.	ΔS	ΔH	ΔG	S_{mix}	ΔS
46	The S_{mix} of _________ is found to 5.76 JK^{-1} mol^{-1}	CO	CO_2	NO	O_2	CO
47	The residual entropy of ________ is 6.23 JK^{-1} mol^{-1}	hydrogen	oxygen	nitrogen	sulphur	hydrogen
48	The ________ of S_{mixed} crystal is given by $-Nk\,[x_a \ln x_a + x_b \ln x_b]$	entropy	enthalpy	internal	Gibbs energy	entropy

49	The residual entropy of hydrogen is due to the existence of ortho form of ___________ in different quantum state.	hydrogen	oxygen	nitrogen	sulphur	hydrogen
50	French scientist Simeon Devis Poisson was discovered by _________ distribution	binomial	poisson	geometric	exponential	binomial
51	The symbol H in the following expression represents	Enthalpy	Entropy	Internal energy	Free energy	Enthalpy
52	The measure of disorder of the molecules of the system is	Enthalpy	Entropy	Gibbs free energy	Helmholtz free energy	Entropy
53	The statement that the total amount of energy in the universe is constant is governed by	First Law of Thermodynamics	Second Law of Thermodynamics	Third Law of thermodynamics	Zeroth Law of Thermodynamics	First Law of Thermodynamics
54	The entropy of a perfectly crystalline structure is Zero. This statement is governed by	First Law of Thermodynamics	Second Law of Thermodynamics	Third Law of thermodynamics	Hess law of constant heat summation	Third Law of thermodynamics
55	Boltzmann ---------- equation is probably the most famous equation in statistical thermodynamics	Gibbs Helmholtz	entropy	enthalpy	Clapeyron	entropy
56	The calorimetric value of entropy in ---------- is 198.0 JK^{-1} mol^{-1}	N_2O	HCl	CO	H_2O	N_2O
57	The spectroscopic value of entropy in -------- is 182.8 JK^{-1} mol^{-1}	NO	N_2O	CO	HCl	NO

58	The calorimetric value of entropy for ---------- is 155.5 JK^{-1} mol^{-1}	NO	N_2O	CO	HCl	CO
59	The calorimetric value for ----------- is 179.8 JK^{-1} mol^{-1}	NO	N_2O	CO	HCl	NO
60	Entropies calculated using the ---------- are called thermal entropies	second law	first law	third law	zeroth law	third law

Third Law of Thermodynamics: Probability and third law. Need for third law. Nernst heat theorem and other forms stating third law. Thermodynamic quantities at absolute zero. Statistical meaning of third law and apparent exception.Mathematical Introduction: Theories of permutation & combination, laws of probability.Distribution laws. Gaussian distribution.

Third law of thermodynamics

The third law of thermodynamics is a statistical law of nature regarding entropy and the impossibility of reaching absolute zero, the null point of the temperature scale. As a system approaches absolute zero, all processes cease and the entropy of the system approaches a minimum value.

This minimum value, the residual entropy, is not necessarily zero, although it is always zero for a perfect crystal in which there is only one possible ground state.

The third law of thermodynamics states that the entropy of a system at absolute zero is a well-defined constant. This is because a system at zero temperature exists in its ground state, so that its entropy is determined only by the degeneracy of the ground state. It means that "it is impossible by any procedure, no matter how idealised, to reduce any system to the absolute zero of temperature in a finite number of operations".

The third law of thermodynamics as stated by Gilbert N. Lewis and Merle Randall:

If the entropy of each element in some (perfect) crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy; but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances.

This version states not only ΔS will reach zero at 0 kelvins, but S itself will also reach zero as long as the crystal has a ground state with only one configuration. Some crystals form defects which causes a residual entropy. This residual entropy disappears when the kinetic barriers to

The statistical-mechanics definition of entropy for a large system:

$$S = k_B \log \Omega$$

where$S$ is entropy, k_B is the Boltzmann constant, and Ω is the number of microstates consistent with the macroscopic configuration.

The third law states that the entropy of most pure substances approaches zero as the absolute temperature approaches zero. This law provides an absolute reference point for the determination of entropy. The entropy determined relative to this point is the absolute entropy.

A special case of this is systems with a unique ground state, such as most crystal lattices. The entropy of a *perfect* crystal lattice as defined by Nernst's theorem is zero (if its ground state is singular and unique, whereby log(1) = 0. An example of a system which does not have a unique ground state is one containing half-integer spins, for which time-reversal symmetry gives two degenerate ground states.This entropy is generally considered to be negligible on a macroscopic scale. Additionally, other exotic systems are known that exhibit geometrical frustration, where the structure of the crystal lattice prevents the emergence of a unique ground state.

The third law of thermodynamics is essentially a statement about the ability to create an *absolute* temperature scale, for which absolute zero is the point at which the internal energy of a solid is precisely 0.

The following three formulations of the third law of thermodynamics:

Need for third law :

1.It is impossible to reduce any system to absolute zero in a finite series of operations.

2.The entropy of a perfect crystal of an element in its most stable form tends to zero as the temperature approaches absolute zero.

3.As temperature approaches absolute zero, the entropy of a system approaches a constant.

Nernst heat theorem

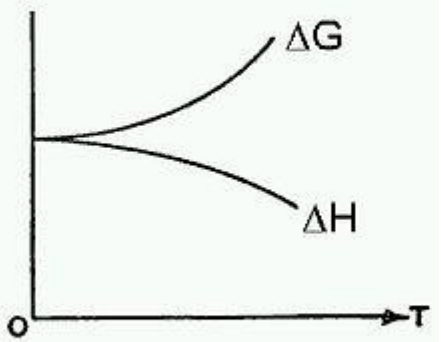
The Nernst heat theorem was formulated by Walther Nernst and was used in the development of the third law of thermodynamics.

The theorem

The Nernst heat theorem says that as absolute zero is approached, the entropy change ΔS for a chemical or physical transformation approaches 0. This can be expressed mathematically as follow

$$\lim_{T\to 0} \Delta S = 0$$

The above equation is a modern statement of the theorem. Nernst often used a form that avoided the concept of entropy.



Graph of energies at low temperatures

The theorem is to start with the definition of the Gibbs free energy (G), G = H - TS, where H stands for enthalpy. For a change from reactants to products at constant temperature and pressure the equation becomes $\Delta G = \Delta H - T\Delta S$.

In the limit of T = 0 the equation reduces to just ΔG = ΔH, which is supported by experimental data. From thermodynamics that the slope of the ΔG curve is -ΔS. Since the slope shown here reaches the horizontal limit of 0 as T → 0 then the implication is that $\Delta S \rightarrow 0$, which is the Nernst heat theorem.

The significance of the Nernst heat theorem is that it was later used by Max Planck to give the third law of thermodynamics, which is that the entropy of all pure, perfectly crystalline homogeneous materials is 0 at absolute zero.

Thermodynamic quantities at Absolute zero :

Absolute zero is the theoretical temperature at which entropy reaches its minimum value. The laws of thermodynamics state that absolute zero cannot be reached using only thermodynamic means.

A system at absolute zero still possesses quantum mechanicalzero-point energy, the energy of its ground state. The kinetic energy of the ground state cannot be removed. However, in the classical interpretation it is zero and the thermal energy of matter vanishes.

Absolute zero is the null point of any thermodynamic temperature scale. It is defined as 0K on the Kelvin scale and as −273.15°C on the Celsius scale. This equates to −459.67°F on the Fahrenheit scale. The temperatures very close to absolute zero, where matter exhibits quantum effects such as superconductivity and superfluidity.

Very low temperatures

The average temperature of the universe due to cosmic microwave background radiation.

Absolute zero cannot be achieved artificially, although it is possible to reach temperatures close to it through the use of cryocoolers. Laser cooling is a technique used to take temperatures to within a billionth of a degree of 0 K. At very low temperatures in the vicinity of absolute zero, matter exhibits many unusual properties including superconductivity, superfluidity, and Bose-Einstein condensation.

At temperatures near 0 K, nearly all molecular motion ceases and, when entropy = S, $\Delta S = 0$ for any adiabatic process. Pure substances can (ideally) form perfect crystals as $T \rightarrow 0$. Max Planck's strong form of the third law of thermodynamics states the entropy of a perfect crystal vanishes at absolute zero. The original Nernst*heat theorem* makes the weaker and less controversial claim that the entropy change for any isothermal process approaches zero as $T \rightarrow 0$:

$$\lim_{T \to 0} \Delta S = 0$$

The implication is that the entropy of a perfect crystal simply approaches a constant value.

The Nernst postulate identifies the isotherm T = 0 as coincident with the adiabat S = 0, although other isotherms and adiabats are distinct. As no two adiabats intersect, no other adiabat can intersect the T = 0 isotherm. Consequently no adiabatic process initiated at nonzero temperature can lead to zero temperature.

It is impossible to reduce the temperature of a system to zero in a finite number of operations. A perfect crystal is one in which the internal lattice structure extends uninterrupted in all directions. The perfect order can be represented by translational symmetry along three (not usually orthogonal) axes. Every lattice element of the structure is in its proper place, whether it is a single atom or a molecular grouping. For substances which have two (or more) stable crystalline forms, such as diamond and graphite for carbon, there is a kind of "chemical degeneracy". The question remains whether both can have zero entropy at $T = 0$ even though each is perfectly ordered.

Perfect crystals never occur in practice; imperfections, and even entire amorphous materials, simply get "frozen in" at low temperatures, so transitions to more stable states do not occur.

Using the Debye model, the specific heat and entropy of a pure crystal are proportional to T^3, while the enthalpy and chemical potential are proportional to T^4. The quantities drop toward their $T = 0$ limiting values and approach with *zero* slopes. Since the relation between changes in Gibbs free energy (G), the enthalpy (H) and the entropy is

$$\Delta G = \Delta H - T\Delta S$$

thus, as T decreases, ΔG and ΔH approach each other (so long as ΔS is bounded). Experimentally, it is found that all spontaneous processes (including chemical reactions) result in a decrease in G as they proceed toward equilbrium. If ΔS and/or T are small, the condition $\Delta G < 0$ may imply that $\Delta H < 0$, which would indicate an exothermic reaction. However, this is not required; endothermic reactions can proceed spontaneously if the $T\Delta S$ term is large enough.

The slopes of the derivatives of ΔG and ΔH converge and are equal to zero at $T = 0$. This ensures that ΔG and ΔH are nearly the same over a considerable range of temperatures. Principle of Thomsen and Berthelot, which states that *the equilibrium state to which a system proceeds is the one which evolves the greatest amount of heat*, i.e. an actual process is the *most exothermic one*.

Statistical meaning of third law :

Statistical mechanics: Alink between quantum mechanics and classical thermodynamics.

Consider a pure crystal all the atoms will be arranged in exact pattern of lattice site

$W = N! / N! = 1$

For similar atoms

$W = N! / N! = 1$, Indistinguishable

For different atoms

$W = N! / n_1!\, n_2!\, n_3!......$ Distinguishable

Boltzmann entropy equation is

$S = k \ln W$

Consider a crystal in which there are 2 atoms A and B

$N_a \rightarrow A$ $\quad\quad$ $N_b \rightarrow B$

$W = N! / N! = N! / n_a!\, n_b!$

S= kln N!/ Na! Nb!

ln N! = NlnN-N

S= k(Nln N-N)- (NalnNa-Na)- (NblnNb-Nb)

S= k (Nln N-N- NalnNa+Na- NblnNb+Nb)

S= k (Nln N-N- NalnNa- NblnNb+N)

S= k (Nln N- NalnNa- NblnNb)

S= -k (NalnNa+ NblnNb- Nln N)

Na= X_aN and Nb= X_bN

S= -k ($X_a\ln X_aN+ X_b\ln X_bN-N\ln N$)

S= -kN ($X_a\ln X_aN+ X_b\ln X_bN-\ln N$)

S= -kN ($X_a\ln X_a+X_a\ln N+X_b\ln X_b+X_b\ln N- \ln N$)

S= -kN ($X_a\ln X_a+X_b\ln X_b+ (X_a+X_b-1) \ln N$)

S= -kN ($X_a\ln X_a+X_b\ln X_b$)

Entropy equation for mixed crystals independent of temperature, so entropy is not zero.

Apparent Exception of third law:

S_{mixing}= -kN ($X_a\ln X_a+X_b\ln X_b$)

Carbonmonoxide,water,nitrous oxide and nitric oxide and Hydrogen do not follow third law.

Carbon Monoxide:

Spectroscopic value of entropy = 160.1 $JK^{-1}mol^{-1}$

Calorimetric value of entropy = 155.5 $JK^{-1}mol^{-1}$

Difference = 4.6 $JK^{-1}mol^{-1}$

Pure crystal of CO CO-CO or COCO

Actual crystal COOCCO or COCOOC

If we imagine CO as mixed crystal in which there is ordered and disordered orientation are present.

S_{mixing}= -kN (1/2 ln1/2 +1/2 ln1/2)

S_{mixing}= -kN (ln1/2) = -Nk (-ln2)

S_{mixing}= -kN ln2 = R ln2

S_{mixing} = 0.693R = 5.76 $JK^{-1}mol^{-1}$

CO ordered and disordered orientation are not present in 1 : 1 ratio.

Nitrous oxide:

Spectroscopic value of entropy = 202.7 $JK^{-1}mol^{-1}$

Calorimetric value of entropy = 198.0 $JK^{-1}mol^{-1}$

Difference = 4.7 $JK^{-1}mol^{-1}$

Actual crystal-ONNONN or NNOONN

Perfect crystal-NNONNO

The ratio is not equal to 1:1, entropy is not equal to zero and do not follow third law of thermodynamics.

Nitric oxide:

Spectroscopic value of entropy = 182.6 $JK^{-1}mol^{-1}$

Calorimetric value of entropy = 179.8 $JK^{-1}mol^{-1}$

Difference = 2.8 $JK^{-1}mol^{-1}$

Actual crystal-NOON or ONON

Perfect crystal-NO-NO-NO

No exist in form of dimers.

Permutation:

In permutation is used with several slightly different meanings, all related to the act of permuting (rearranging in an ordered fashion) objects or values. Informally, a permutation of a set of values is an arrangement of those values into a particular order. Thus there are six permutations of the set {1,2,3}, namely [1,2,3], [1,3,2], [2,1,3], [2,3,1], [3,1,2], and [3,2,1].

Apermutation of a set*S* is defined as a bijection from *S* to itself (i.e., a map*S* → *S* for which every element of *S* occurs exactly once as image value). To such a map *f* is associated the rearrangement of *S* in which each element *s* takes the place of its image *f*(*s*). In combinatorics, a permutation of a finite set *S* is defined as an ordering of its elements into a list. In this sense, the permutations of *S* differ precisely by a rearrangement of their elements. For a set *S* that is given with an initial ordering, such as *S*={1,2,3,...,*n*}, these two meanings can be almost identified: applying a permutation in the first sense to this initial ordering gives an alternative ordering of the elements, which is a permutation in the second sense.

The rule to determine the number of permutations of *n* objects was known.

The product of multiplication of the arithmetical series beginning and increasing by unity and continued to the number of places, will be the variations of number with specific figures.

Permutations :

A permutation of ***n*** taken ***m*** at a time is defined as an ordered selection of ***m*** out of the ***n*** items. The total number of all the possible permutations is denoted as:

$$P_m^n = n(n-1)(n-2)\cdots(n-m+1) \quad \text{where } n \geq m.$$

Combinations :

A combination of ***n*** taken ***m*** at a time is defined as a selection of ***m*** out of the ***n*** items without regard to the order. The total number of all the possible combinations is denoted as:

$$C_m^n = \frac{n!}{m!(n-m)!} = \binom{n}{m} = \binom{n}{n-m} \quad \text{where } n \geq m$$

Addition Law of Probability

Theorem

Let $\Pr$ be a probability measure on an event space Σ.

Let $A, B \in \Sigma$.

Then:

$$\Pr(A \cup B) = \Pr(A) + \Pr(B) - \Pr(A \cap B)$$

That is, the probability of either eventoccurring equals the sum of their individual probabilities less the probability of them both occurring.

This is known as the **addition law of probability**, or the **sum rule**.

Proof

By definition, a probability measure is a measure.

Hence, again by definition, it is a countably additive function.

By Measure is Finitely Additive Function, we have that $\Pr$is an additive function.

So we can apply Additive Function on Union of Sets directly.

Alternative Proof

Alternatively, we can prove it directly, although it works out exactly the same:

From Set Difference and Intersection form Partition, we have that:

$A$is the union of the two disjoint sets$A \setminus B$and $A \cap B$;

$B$is the union of the two disjoint sets$B \setminus A$and $A \cap B$.

So, by the definition of probability measure:

$$\Pr(A) = \Pr(A \setminus B) + \Pr(A \cap B);$$

$$\Pr(B) = \Pr(B \setminus A) + \Pr(A \cap B)$$

We also have from Set Difference Disjoint with Reversethat $(A \setminus B) \cap (B \setminus A) = \varnothing$.

Hence:

$$\begin{aligned} \Pr(A) + \Pr(B) &= \Pr(A \setminus B) + 2\Pr(A \cap B) + \Pr(B \setminus A) \\ &= \Pr((A \setminus B) \cup (A \cap B) \cup (B \setminus A)) + \Pr(A \cap B\ B) \\ &= \Pr(A \cup B) + \Pr(A \cap B) \end{aligned}$$

Multiplicative Law of Probability:

- The probability of the intersection of two events A and B is
- P(A \ B) = P(A)P(BjA)= P(B)P(AjB)
- If A and B are independent, the P(A\B) = P(A)P(B).
- The Multiplicative Law of Probability is often used to determine the probability of an event which involves a sequence of random occurances.

Normal distribution

In probability theory, the **normal** (or **Gaussian**) **distribution**, is a continuous probability distribution that is often used as a first approximation to describe real-valued random variables that tend to cluster around a single mean value. The graph of the associated probability density function is "bell"-shaped, and is known as the *Gaussian function* or *bell curve*.

$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}}\, e^{-\frac{(x-\mu)^2}{2\sigma^2}},$$

where parameter μ is the *mean* (location of the peak) and σ^2 is the *variance* (the measure of the width of the distribution). The distribution with $\mu = 0$ and $\sigma^2 = 1$ is called the **standard normal**.

The normal distribution is considered the most “basic” continuous probability distribution due to its role in the central limit theorem, and is one of the first continuous distributions. Specifically, by the central limit theorem, under certain conditions the sum of a number of random variables with finite means and variances approaches a normal distribution as the number of variables increases. For example, the observational error in an experiment is usually assumed to follow a normal distribution, and the propagation of uncertainty is computed using this assumption.

A normally-distributed variable has a symmetric distribution.

- The normal distribution is the only absolutely continuous distribution all of whose cumulants beyond the first two (i.e. other than the mean and variance) are zero.
- For a given mean and variance, the corresponding normal distribution is the continuous distribution with the maximum entropy.

Definition

The simplest case of a normal distribution is known as the *standard normal distribution*, described by the probability density function

$$\phi(x) = \frac{1}{\sqrt{2\pi}}\, e^{-\frac{1}{2}x^2},$$

The constant $1/\sqrt{2\pi}$ in this expression ensures that the total area under the curve $\phi(x)$ is equal to one, and $\frac{1}{2}$ in the exponent makes the “width” of the curve (measured as half of the distance between the inflection points of the curve) also equal to one. In statistics to denote this function with the Greek letter ϕ (phi), whereas density functions for all other distributions are usually denoted with letters f or p. The alternative glyph φ is also used quite often, “φ” to denote characteristic functions.

A normal distribution results from exponentiating a quadratic function (just as an exponential distribution results from exponentiating a linear function):

$$f(x) = e^{ax^2+bx+c}.$$

This yields the classic “bell curve” shape (provided that $a < 0$ so that the quadratic function is concave). Note that $f(x) > 0$ everywhere. One can adjust a to control the “width” of the bell, then adjust b to move the central peak of the bell along the x-axis, and finally adjust c to control the “height” of the bell. For $f(x)$ to be a true probability density function over **R**, one must choose c such that $\int_{-\infty}^{\infty} f(x)\,dx = 1$(which is only possible when $a < 0$).

Rather than using a, b, and c, it is far more common to describe a normal distribution by its mean$\mu = -b/(2a)$ and variance$\sigma^2 = -1/(2a)$. Changing to these new parameters rewrite the probability density function in a convenient standard form,

$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}}\, e^{\frac{-(x-\mu)^2}{2\sigma^2}} = \frac{1}{\sigma}\,\phi\!\left(\frac{x-\mu}{\sigma}\right).$$

For a standard normal distribution, $\mu = 0$ and $\sigma^2 = 1$. The last part of the equation above shows that any other normal distribution can be regarded as a version of the standard normal distribution that has been stretched horizontally by a factor σ and then translated rightward by a distance μ. Thus, μ specifies the position of the bell curve’s central peak, and σ specifies the “width” of the bell curve.

The parameter μ is at the same time the mean, the median and the mode of the normal distribution. The parameter σ^2 is called the *variance*; as for any random variable, it describes how concentrated the distribution is around its mean. The square root of σ^2 is called the *standard deviation* and is the width of the density function.

The normal distribution is usually denoted by $N(\mu, \sigma^2)$. Commonly the letter N is written in calligraphic font Thus when a random variable X is distributed normally with mean μ and variance σ^2, we write

$$X \sim \mathcal{N}(\mu, \sigma^2).$$

Alternative formulations

σ^2 use its reciprocal $\tau = \sigma^{-2}$ (or $\tau = \sigma^{-1}$), which is called the precision. This parameterization has an advantage in numerical applications where σ^2 is very close to zero and is more convenient to work with in analysis as τ is a natural parameter of the normal distribution. Another advantage of using this parameterization is in the study of conditional distributions in multivariate normal case.

The normal distribution should be called the "*standard*" the standard normal was considered to be the one with variance σ^2

$$f(x) = \frac{1}{\sqrt{\pi}}\, e^{-x^2}$$

The standard normal with variance σ^2

$$f(x) = e^{-\pi x^2}$$

Characterization

The normal distribution was defined by specifying its probability density function.

Probability density function

The probability density function (pdf) of a random variable describes the relative frequencies of different values for that random variable. The pdf of the normal distribution is given by the formula

$$f(x;\,\mu,\sigma^2) = \frac{1}{\sqrt{2\pi\sigma^2}}\, e^{-(x-\mu)^2/(2\sigma^2)} = \frac{1}{\sigma}\,\phi\!\left(\frac{x-\mu}{\sigma}\right), \qquad x \in \mathbb{R}.$$

This is a proper function only when the variance σ^2 is not equal to zero. This is a continuous smooth function, defined on the entire real line, and which is called the "Gaussian function".

Properties:

- Function $f(x)$ is symmetric around the point $x = \mu$, which is at the same time the mode, the median and the mean of the distribution.

- The inflection points of the curve occur one standard deviation away from the mean (i.e., at $x = \mu - \sigma$ and $x = \mu + \sigma$).
- The standard normal density $\phi(x)$ is an eigenfunction of the Fourier transform.
- The function is supersmooth of order 2, implying that it is infinitely differentiable.
- The first derivative of $\phi(x)$ is $\phi'(x) = -x\cdot\phi(x)$; the second derivative is $\phi''(x) = (x^2 - 1)\phi(x)$. More generally, the n-th derivative is given by $\phi^{(n)}(x) = (-1)^n H_n(x)\phi(x)$, where H_n is the Hermite polynomial of order n.

When $\sigma^2 = 0$, the density function doesn't exist. Ageneralized function that defines a measure on the real line, and it can be used to calculate, for example, expected value is

$$f(x;\, \mu, 0) = \delta(x - \mu).$$

where$\delta(\cdot)$is the Dirac delta function which is equal to infinity at $x = 0$.

The property 1, it is possible to relate all normal random variables to the standard normal. For example if X is normal with mean μ and variance σ^2, then

$$Z = \frac{X - \mu}{\sigma}$$

has mean zero and unit variance, that is Z has the standard normal distribution. A standard normal random variable Z can always construct another normal random variable with specific mean μ and variance σ^2:

$$X = \sigma Z + \mu.$$

$$F_X(x) = \Phi\left(\frac{x - \mu}{\sigma}\right), \quad f_X(x) = \frac{1}{\sigma}\,\phi\left(\frac{x - \mu}{\sigma}\right).$$

	Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answers
1	The equation of average speed for Maxwell distribution is -----------	$\sqrt{8RT/\pi M}$	$\sqrt{2RT/M}$	$\sqrt{3RT/M}$	$\sqrt{5RT/\pi M}$	$\sqrt{8RT/\pi M}$
2	The equation for average square speed of Maxwell distribution is -----------	$\sqrt{2RT/M}$	$\sqrt{5RT/\pi M}$	$\sqrt{8RT/\pi M}$	$\sqrt{3RT/M}$	$\sqrt{3RT/M}$
3	The equation for most probable speed of Maxwell distribution is -----------	$\sqrt{8RT/\pi M}$	$\sqrt{2RT/M}$	$\sqrt{5RT/\pi M}$	$\sqrt{3RT/M}$	$\sqrt{2RT/M}$
4	The equation for Root Mean Square Speed of Maxwell distribution is -----------	$\sqrt{2RT/\pi M}$	$\sqrt{3RT/M}$	$\sqrt{8RT/\pi M}$	$\sqrt{5RT/\pi M}$	$\sqrt{3RT/M}$
5	In equiparttion law each of quadratic term contributes ______ to the average energy.	1/2kT	4/2kT	5/2kT	7/2kT	1/2kT
6	The equation for Stirlings approximation is ___________	$\ln N! = N \ln N - N$	$\ln N!$	$\ln N! - \ln N$	$\ln N! = N \ln N + N$	$\ln N! = N \ln N - N$
7	The state of maximum thermodynamic probability equation is ________	$e-\alpha = N/S$	$Ni = e- \alpha$	$Ni = N/S$	$e\alpha = N/S$	$Ni = N/S$

8	The Maxwell Boltzmann distribution law equation is______	Ni = gi. e-α e-βεί	Ni = gi. e-α eβεί	Ni = gi. eα e-βεί	Ni = gi. eα eβεί	Ni = gi. e-α e-βεί
9	The number of molecules occupying particular energy level of particular quantum state of Maxwell distribution law equation is _______	Nij = eα eβεί	Nij= e-α e-βεί	Nij= e-α eβεί	Nij = eα e-βεί	Nij= e-α e-βεί
10	The molecular partition function q is given by ________	q = ∑gi. e-βεί	q = ∑gi. e-βεί	q =∑ e-βεί	q =∑ eβεί	q = ∑gi. e-βεί
11	The equation for the evaluation of α in M.B.distribution law is ________	e-α=N/q	e-α=N/S	Ni =e- α	eα=N/S	e-α=N/q
12	The equation for the evaluation of β in M.B.distribution law is ________	β = 1/kT	β = -1/kT	β = kT	β = 2/kT	β = 1/kT
13	The equation for M.B.distribution of molecular velocity for evaluation of constant A is ________	A =(b/2π)1/2	A =(- b/2π)1/2	A =(b/2π)5/2	A =(- b/2π)3/2	A =(- b/2π)1/2
14	The Maxwell speed distribution equation is __________	(m/2π kT)1/2.e-mc/2kT.4πc2.dc	(m/2π kT)3/2.e-mc/2kT. dvx.dvy.dvz	(m/2π kT)3/2.e-mc/2kT.4πc2.dc	(m/2π kT)3/2.emc/2kT.4πc2 .dc	(m/2π kT)3/2.e-mc/2kT.4πc2.dc

15	The Maxwell distribution of molecular velocity equation is __________	(m/2π kT)1/2.e-mc/2kT.4πc2.dc	(m/2π kT)3/2.e-mc/2kT. dvx.dvy.dvz	(m/2π kT)3/2.emc/2kT.4πc2.dc	(m/2π kT)3/2.emc/2kT. dvx.dvy.dvz	(m/2π kT)3/2.e-mc/2kT. dvx.dvy.dvz
16	The Maxwell distribution law in terms of kinetic translational energy equation is __________	dNεtr /N =(1/ kT) 3/2 .(εtr / π)1/2.2e- ε tr /kT.dεtr	dNεtr /N =(1/ kT) 5/2 .(εtr / π) 1/2.2e- ε tr /kT.dεtr	dNεtr /N =(1/ kT) 3/2 .(εtr / π) 3/2.2e- ε tr /kT.dεtr	dNεtr /N =(1/ kT) 3/2 .(εtr / π) 5/2..2e- ε tr /kT.dεtr	dNεtr /N =(1/ kT) 3/2 .(εtr / π)1/2.2e- ε tr /kT.dεtr
17	The equation for various kinds of speed is Cmp : < C> :<C2>	√2RT /M : √8RT /πM : √3RT /M	√8RT /πM : √2RT /M : √3RT /M	√3RT /M : √8RT /πM : √2RT /M	√3RT /πM : √8RT /πM : √2RT /M	√2RT /M : √8RT /πM : √3RT /M
18	The ratio of various kinds of speed is Cmp : < C> :<C2>1/2	1.128:1.225:1	1.128:1:1.225	1.225:1:1.128	1:1.128:1.225	1:1.128:1.225
19	The average square speed <C2>1/2 value is ________	1.128	1.225	1	1.228	1.225
20	The most probable speed Cmp value is _______	1.128	1.225	1	1.228	1
21	The average speed < C> value is _______	1.128	1	1.228	1.225	1.128
22	The RMS speed <C2>1/2 value is ________	1.128	1	1.225	1.228	1.225
23	The rotational contribution to Cv for a polyatomic molecule in linear molecule is ________	Cv (rot)=R	Cv (rot)=3/2 R	Cv (rot)=3R	Cv (rot)=5R	Cv (rot)=R

24	The rotational contribution to Cv for a polyatomic molecule in non -linear molecule is ________	Cv (rot)=R	Cv (rot)=3/2 R	Cv (rot)=3R	Cv (rot)=5R	Cv (rot)=3/2 R
25	The number of vibrational degrees of freedom in linear molecule is_______	3 N-5	3 N-6	3 N-4	3 N-7	3 N-5
26	The number of vibrational degrees of freedom in non- linear molecule is_______	3 N-5	3 N-4	3 N-6	3 N-7	3 N-6
27	The equation for polyatomic gas in non-linear molecule is ________	Cv=3/2 R+3/2 R+ (3N-5)R	Cv=3/2 R+3/2 R+ (3N-6)R	Cv=3/2 R+R+ (3N-5)R	Cv=3/2 R+3R+ (3N-5)R	Cv=3/2 R+3/2 R+ (3N-6)R
28	The equation for polyatomic gas in linear molecule is ________	Cv=3/2 R+R+ (3N-5)R	Cv=3/2 R+3/2 R+ (3N-6)R	Cv=3/2 R+3/2 R+ (3N-5)R	Cv=3/2 R+3R+ (3N-5)R	Cv=3/2 R+R+ (3N-5)R
29	The equation for monoatomic gas is ________	Cv=3/2 R	Cv=R	Cv=5/2 R	Cv=5R	Cv=3/2 R
30	Planck proposed the relationship between the entropy of a system and the thermodynamic probability is given by the equation _______	S=klnw	-S=klnw	S= -klnw	S=klnT	S=klnw
31	The equation for M.B.distribution law of molecular velocity is ___________	A=(m/2π kT)1/2	A=(m/2π kT)5/2	A=(-m/2π kT)5/2	A=(-m/2π kT)3/2	A=(m/2π kT)1/2

32	$\sqrt{3RT/M}$ equation of Maxwell distribution law is _________	average square speed	most probable speed	average speed	partition function	average square speed
33	$\sqrt{2RT/M}$ equation of Maxwell distribution law is _________	average speed	most probable speed	average square speed	equipartition	most probable speed
34	$\sqrt{8RT/\pi M}$ equation of Maxwell distribution law is _________	most probable speed	average square speed	average speed	root mean square speed	average speed
35	$\sqrt{3RT/M}$ equation of Maxwell distribution law is _________	average speed	most probable speed	root mean square speed	partition function	root mean square speed
36	1.128 value belongs to __________	average speed	average square speed	most probable speed	root mean square speed	average speed
37	1.225 value belongs to __________	average speed	average square speed	most probable speed	partition function	average square speed
38	The value of 1 belongs to _________	average speed	average square speed	most probable speed	root mean square speed	most probable speed
39	In speed distribution higher molecular weight increases as ________	volume increases	volume decreases	volume increasing with decreasing	volume decreasing with increasing.	volume increases
40	In speed distribution as molecular weight _________the disribution curve broadens.	increases	decreases	volume increasing with decreasing	volume decreasing with increasing.	decreases

41	The equation of _________ for Maxwell distribution is $\sqrt{8RT/\pi M}$	average speed	average square speed	most probable speed	root mean square speed	average speed
42	The equation for __________ of Maxwell distribution is $\sqrt{3RT/M}$	average speed	average square speed	most probable speed	partition function	average square speed
43	The equation for __________ of Maxwell distribution is $\sqrt{2RT/M}$	average speed	average square speed	most probable speed	root mean square speed	most probable speed
44	The equation for _______ of Maxwell distribution is $\sqrt{3RT/M}$	average speed	root mean square speed	most probable speed	partition function	root mean square speed
45	The equation ln N! =N ln N –N __________ represents ?	Stirlings approximation	partition function	equipartition law	Maxwell boltzmann distribution law	Stirlings approximation
46	The equation Ni =N/S _______	state of maximum thermodynamic probability	Stirlings approximation	partition function	equipartition law	state of maximum thermodynamic probability
47	The equation for Cv=3/2 R is ________	monoatomic gas	diatomic gas	polyatomic gas	state of maximum thermodynamic probability	monoatomic gas
48	The value of _______ belongs to most probable speed	1	1.225	1.128	2.25	1
49	The number of _________ degrees of freedom in linear molecule is 3N-5	rotational	vibrational	translational	electronic	vibrational

50	The number of _________ degrees of freedom in non- linear molecule is 3N-6	rotational	vibrational	translational	electronic	vibrational
51	In speed distribution higher molecular weight --------- as volume increases .	decreases	increases	volume increasing with decreasing	volume decreasing with increasing	increases
52	The average kinetic energy of the gas molecules is	inversely proportional to its absolute temperature	directly proportional to its absolute temperature	equal to the square of its absolute temperature		directly proportional to its absolute temperature
53	For one mole of a gas the kinetic energy is given by	E = 1/2 RT	E = 3/2 RT	E = 5/2 RT	E = 7/2 RT	E = 3/2 RT
54	The equation monoatomic --------- gas is Cv=3/2 R	monoatomic	diatomic	polyatomic	triatomic	monoatomic
55	----------- proposed the relationship between the entropy of a system and the thermodynamic probability is given by the equation S=k ln w	Debye	Maxwell Boltzmann	Planck	Clapeyron	Planck
56	Law of distribution of velocities was given by---------	Maxwell	Clausius	Bernoulii	Dalton	Maxwell
57	In determining kinetic equation of gases the velocity of all molecules are not equal so we use -----------	square of velocity	mean square velocity	under root of velocity	cube of velocity	mean square velocity

58	The example of gas having monoatomic molecules is --------	Nitrogen	hydroge	neon and argon	oxygen and nitrogen	neon and argon
59	At constant temperature, the pressure of the gas is reduced to one third, the volume	reduces to one third	increases by three times	remains the same	cannot be predicted	increases by three times
60	For one mole of a gas, the ideal gas equation is	PV = RT	PV = 1/2 RT	PV = 3/2 RT	PV = 5/2 RT	PV = RT

UNIT – III

SYLLABUS

Maxwell distribution law for molecular velocities and molecular speeds in an ideal gas. Velocity and speed distribution functions. Experimental verification of Maxwell distribution law. Evaluation of average speed, root mean square speed and most probable speed from distribution law. Distribution function in terms of the kinetic energy of an ideal gas. The principle of equipartition of energy and the calculation of heat capacities of ideal gases. Limitations of the principle of equipartition of energy.

Quantum statistics: Maxwell-Boltzmann statistics. Thermodynamic probability. Thermodynamic probabilities of systems in equilibrium. Boltzmann expression for entropy. Stirling's approximation. State of maximum thermodynamics probability. Legrangian multipliers. Thermodynamic probabilities of systems involving energy levels. Maxwell-Boltzmann distribution law. Evaluation of alpha and beta in MB distribution law.

Maxwell–Boltzmann distribution

The Maxwell–Boltzmann distribution describes particle speeds in gases, where the particles do not constantly interact with each other but move freely between short collisions. It describes the probability of a particle's speed (the magnitude of its velocity vector) being near a given value as a function of the temperature of the system, the mass of the particle, and that speed value. This probability distribution is named after James Clerk Maxwell and Ludwig Boltzmann.

The Maxwell–Boltzmann distribution is usually for the distribution of molecular speeds, velocities, momenta, and magnitude of the momenta of the molecules, each of which will have a different probability distribution function. "Maxwell–Boltzmann distribution" refer to the distribution of speed. This distribution can be thought of as the magnitude of a 3-dimensional vector whose components are independent and normally distributed with mean 0 and standard deviation$a$. If X_i are distributed as $X \sim N(0, a^2)$, then

$$Z = \sqrt{X_1^2 + X_2^2 + X_3^2}$$

is distributed as a Maxwell–Boltzmann distribution with parameter a. Apart from the scale parameter a, the distribution is identical to the chi distribution with 3 degrees of freedom.

The Maxwell–Boltzmann distribution applies to ideal gases close to thermodynamic equilibrium, negligible quantum effects, and non-relativistic speeds. It forms the basis of the kinetic theory of gases, which explains many fundamental gas properties, including pressure and diffusion.

Derivation

The derivation by Maxwell assumed all three directions would behave in the same fashion, but a later derivation by Boltzmann dropped this assumption using kinetic theory. The Maxwell–Boltzmann distribution can be derived from the Boltzmann distribution for energies.

$$\frac{N_i}{N} = \frac{g_i \exp\left(-E_i/kT\right)}{\sum_j g_j \exp\left(-E_j/kT\right)} \qquad (1)$$

where N_i is the number of molecules at equilibrium temperature T, in a state i which has energy E_i and degeneracy g_i, N is the total number of molecules in the system and k is the Boltzmann constant. (Sometimes the above equation is written without the degeneracy factor g_i. In this case the index i will specify an individual state, rather than a set of g_i states having the same energy E_i.) Because velocity and speed are related to energy, Equation 1 can be used to derive relationships between temperature and the speeds of molecules in a gas. The denominator in this equation is known as the canonical partition function.

For the case of an "ideal gas" consisting of non-interacting atoms in the ground state, all energy is in the form of kinetic energy, and g_i is constant for all i. The relationship between kinetic energy and momentum for massive particles is

$$E = \frac{p^2}{2m} \qquad (2)$$

where p^2 is the square of the momentum vector **p** = [p_x, p_y, p_z]. Rewrite Equation 1 as:

$$\frac{N_i}{N} = \frac{1}{Z} \exp\left[-\frac{p_{i,x}^2 + p_{i,y}^2 + p_{i,z}^2}{2mkT}\right] \qquad (3)$$

where Z is the partition function, corresponding to the denominator in Equation 1. Here m is the molecular mass of the gas, T is the thermodynamic temperature and k is the Boltzmann constant. This distribution of N_i/N is proportional to the probability density function$f_\mathbf{p}$ for finding a molecule with these values of momentum components, so:

$$f_\mathbf{p}(p_x, p_y, p_z) = \frac{c}{Z} \exp\left[-\frac{p_x^2 + p_y^2 + p_z^2}{2mkT}\right]. \qquad (4)$$

The normalizing constant$c$, can be determined by recognizing that the probability of a molecule having *any* momentum must be 1. Therefore the integral of equation 4 over all p_x, p_y, and p_z must be 1.

It can be shown that:

$$c = \frac{Z}{(2\pi mkT)^{3/2}}. \qquad (5)$$

Substituting Equation 5 into Equation 4 gives:

$$f_\mathbf{p}(p_x, p_y, p_z) = \left(\frac{1}{2\pi mkT}\right)^{3/2} \exp\left[-\frac{p_x^2 + p_y^2 + p_z^2}{2mkT}\right]. \qquad (6)$$

The distribution is the product of three independent normally distributed variables p_x, p_y, and p_z, with variance mkT. Additionally,the magnitude of momentum will be distributed as a Maxwell–Boltzmann distribution, with a= √mkTThe Maxwell–Boltzmann distribution for the momentum (or equally for the velocities) can be obtained using the H-theorem at equilibrium within the kinetic theory.

Distribution for the energy

Using $p^2 = 2mE$, and the distribution function for the magnitude of the momentum, we get the energy distribution:

$$f_E\,dE = f_p\left(\frac{dp}{dE}\right)\,dE = 2\sqrt{\frac{E}{\pi(kT)^3}}\;\exp\left[\frac{-E}{kT}\right]\,dE. \qquad (7)$$

Since the energy is proportional to the sum of the squares of the three normally distributed momentum components, this distribution is a chi-square distribution with three degrees of freedom:

$$f_E(E)\,dE = \chi^2(x;3)\,dx$$

where

$$x = \frac{2E}{kT}.$$

By the equipartition theorem, this energy is evenly distributed among all three degrees of freedom, so that the energy per degree of freedom is distributed as a chi-square distribution with one degree of freedom:

$$f_\epsilon(\epsilon)\,d\epsilon = \sqrt{\frac{\epsilon}{\pi kT}}\;\exp\left[\frac{-\epsilon}{kT}\right]\;d\epsilon$$

where ε is the energy per degree of freedom. At equilibrium, this distribution will hold true for any number of degrees of freedom. For example, if the particles are rigid mass dipoles, they will have three translational degrees of freedom and two additional rotational degrees of freedom. The energy in each degree of freedom will be described according to the above chi-square distribution with one degree of freedom, and the total energy will be distributed according to a chi-square distribution with five degrees of freedom.

Distribution for the velocity vector

The velocity probability density $f_\mathbf{v}$ is proportional to the momentum probability density function by

$$f_\mathbf{v} d^3v = f_\mathbf{p} \left(\frac{dp}{dv}\right)^3 d^3v$$

and using **p** = m**v** we get

$$f_\mathbf{v}(v_x, v_y, v_z) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2kT}\right],$$

which is the Maxwell–Boltzmann velocity distribution. The probability of finding a particle with velocity in the infinitesimal element [dv_x, dv_y, dv_z] about velocity **v** = [v_x, v_y, v_z] is

$$f_\mathbf{v}\left(v_x, v_y, v_z\right)\, dv_x\, dv_y\, dv_z.$$

Like the momentum, this distribution is seen to be the product of three independent normally distributed variables v_x, v_y, and v_z, but with variance $\frac{kT}{m}$. It can also be seen that the Maxwell–Boltzmann velocity distribution for the vector velocity [v_x, v_y, v_z] is the product of the distributions for each of the three directions:

$$f_v\left(v_x, v_y, v_z\right) = f_v(v_x) f_v(v_y) f_v(v_z)$$

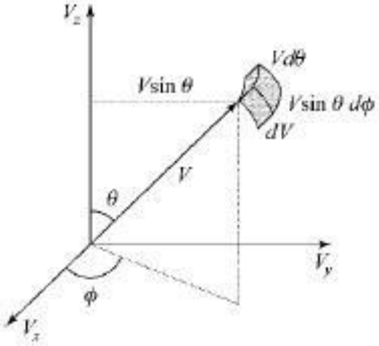
where the distribution for a single direction is

$$f_v(v_i) = \sqrt{\frac{m}{2\pi kT}} \exp\left[\frac{-mv_i^2}{2kT}\right].$$

Each component of the velocity vector has a normal distribution with mean $\mu_{v_x} = \mu_{v_y} = \mu_{v_z} = 0$ and standard deviation $\sigma_{v_x} = \sigma_{v_y} = \sigma_{v_z} = \sqrt{\frac{kT}{m}}$, so the vector has a 3-dimensional normal distribution, also called a "multinormal" distribution, with mean $\mu_{\mathbf{v}} = \mathbf{0}$ and standard deviation $\sigma_{\mathbf{v}} = \sqrt{\frac{3kT}{m}}$.

The Maxwell–Boltzmann Speed Distribution

The Maxwell–Boltzmann velocity distribution accounts for both the speed and direction of assembly particles,we are often interested more in their speed than in their direction. For this purpose, it proves convenient to introduce spherical coordinates in *velocity space*.



Spherical velocity space

The Maxwell–Boltzmann distribution for the speed follows the distribution of the velocity vector. The speed is

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

and the volume is

$$dv_x\,dv_y\,dv_z = v^2 \sin\theta\,dv\,d\theta\,d\varphi$$

where θ and φ are the "course" and "path angle". Integration of the normal probability density function of the velocity, (from 0 to 2π and path angle (from $-\pi/2$ to $\pi/2$), with substitution of the speed for the sum of the squares of the vector components, yields the probability density function.

Cartesian to spherical coordinates can be accomplished by invoking the transformation

$$dV_x\,dV_y\,dV_z = (V d\theta)(V \sin\theta\,d\phi)(dV) = V^2 \sin\theta\,dV d\theta\,d\phi \tag{1}$$

where V is the particle speed, θ is the zenith angle, and ϕ is the azimuthal angle in spherical

velocity space. The speed PDF can now be determined from the velocity PDF by converting to spherical velocity coordinates and then integrating over all possible solid angles. Converting first to spherical coordinates, we

obtain, from Eq. (1),

$$f(\mathbf{V})\,dV_x\,dV_y\,dV_z = f(\mathbf{V})\,V^2 \sin\theta\,dV d\theta\,d\phi$$

For an isotropic velocity distribution, $f(\mathbf{V})$ is unaffected by either θ or φ; thus, directly integrating over all zenith and azimuthal angles, we find that

$$f(V)\,dV = f(\mathbf{V})\,V^2 dV \int_0^{\pi} \sin\theta\,d\theta \int_0^{2\pi} d\phi = 4\pi V^2 f(\mathbf{V})\,dV \tag{2}$$

where $f(V)$ represents the derived speed PDF.

From Eq. (2), we observe that the PDF for any isotropic velocity distribution canbe converted to its corresponding speed PDF by employing

$$f(V) = 4\pi V^2 f(\mathbf{V}) \tag{3}$$

Hence, substituting from Eq. (3), we determine the PDF representing the *Maxwell–Boltzmann speed distribution* as

$$f(V) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT}\right)^{3/2} V^2 \exp\left(-\frac{mV^2}{2kT}\right) \tag{4}$$

This Maxwell distributionequation with distribution parameter $a = \sqrt{\frac{kT}{m}}$.

The mean speed, most probable speed (mode), and root-mean-square can be obtained from properties of the Maxwell distribution.

Speed is defined as $u = \frac{v}{v_p}$, where $v_p = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}$ is the most probable speed. The distribution of speeds allows comparison of dissimilar gasses, independent of temperature and molecular weight.

The **most probable speed**, v_p, is the speed possessed by any molecule (of the same mass *m)* in the system and corresponds to the maximum value or mode of $f(v)$. Calculate df/dv, set it to zero and solving for v:

$$\frac{df(v)}{dv} = 0$$

$$v_p = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}$$

Where R is the gas constant and $M = N_A m$ is the molar mass of the substance.

The most probable speed can be determined by implementing

$$\frac{df(V)}{dV} = 0,$$

from which we obtain

$$V_{mp} = \left(\frac{2kT}{m}\right)^{1/2}. \quad (5)$$

Consequently, Eq. (4) can be reformulated as

$$f(V) = \frac{4}{\sqrt{\pi} V_{mp}} \left(\frac{V}{V_{mp}}\right)^2 \exp\left[-\left(\frac{V}{V_{mp}}\right)^2\right] \quad (6)$$

which is clearly non-Gaussian compared to $f(Vx)$.

The speed PDF for a gaseous assembly, the mean for any function of particlespeed, $G(V)$, can be determined by evaluating

$$\overline{G(V)} = \int_0^\infty G(V) f(V)\, dV .$$

Therefore, for $G(V) = Vn$, from Eq. (6) we obtain

$$\overline{V^n} = \frac{4}{\sqrt{\pi}} \left(\frac{2kT}{m}\right)^{n/2} \int_0^\infty \left(\frac{V}{V_{mp}}\right)^{n+2} \exp\left[-\left(\frac{V}{V_{mp}}\right)^2\right] d\left(\frac{V}{V_{mp}}\right) \quad (7)$$

Applying the Gaussian integrals , we find that the mean and rootmean-square speeds for a given assembly temperature become

$$\overline{V} = \left(\frac{8kT}{\pi m}\right)^{1/2} \quad (8)$$

$$V_{rms} = \sqrt{\overline{V^2}} = \left(\frac{3kT}{m}\right)^{1/2} \quad (9)$$

Comparing Eqs. (5), (8), and (9), we see that, at translational equilibrium,

$$V_{rms} > \overline{V} > V_{mp}$$

which confirms the non-Gaussian nature of the speed PDF for Maxwell–Boltzmannstatistics.

The mean speed is the mathematical average of the speed distribution

$$\langle v \rangle = \int_0^\infty v\, f(v)\, dv = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} = \frac{2}{\sqrt{\pi}} v_p$$

The root mean square speed, v_{rms} is the square root of the average squared speed:

$$v_{\mathrm{rms}} = \left(\int_0^\infty v^2 f(v)\, dv\right)^{1/2} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3}{2}} v_p$$

The typical speeds are related as follows:

$$0.886\langle v\rangle = v_p < \langle v\rangle < v_{\mathrm{rms}} = 1.085\langle v\rangle.$$

The **Maxwell speed distribution (MSD)**, is a probability distribution describing the "spread" of these molecular speeds; it is derived, and therefore only valid, assuming that with an ideal gas. The speed is a scalar quantity, describing how fast the particles are moving, regardless of direction; velocity also describes the direction that the particles are moving. Another important element is that space is three dimensional, for any given speed, there are many possible velocity vectors.

The probability of a molecule having a given speed can be found by using Boltzmann factor; considering the energy to be dependent only on the kinetic energy:

$$(\text{probability of a molecule having speed between v and } v{+}dv) \propto e^{-mv_x^2/(2kT)}.$$

Here, *m* is the mass of the molecule, *k* is Boltzmann's constant, and *T* is the temperature.

The above equation gives the probability that one component of particle's velocity v_x. In 3 dimension we need to count particles that has all possible combinations of $\{v_x,v_y,v_z\}$ results in $v^2 = v_x^2 + v_y^2 + v_z^2$. In other words, to sum all potential combinations of individual components in 3 dimensional velocity space so that their vector some is desired value. For the distribution in 3 dimension, integrate above equations in dv_x,dv_y,dv_z over entire velocity space such that component sum is constant. If the particles with speed v in a 3-dimensional velocity space, theseparticles lie on the surface of a sphere with radius *v*. The larger *v* is, the bigger the sphere, and the more possible velocity vectors. So the number of possible velocity vectors for a given speed goes like the surface area of a sphere of radius *v*.

$$(\text{number of vectors corresponding to speed } v) \propto 4\pi v^2.$$

Multiplying these two functions together gives us the distribution, and normalising this gives us the MSD in its entirety.

$$D(v)\,dv = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-mv^2/(2kT)}\,dv.$$

(Again, m is the mass of the molecule, k is Boltzmann's constant, and T is the temperature.)

This formula is a normalised probability distribution, it gives the probability of a molecule having a speed between v and $v + dv$. The probability of a molecule having a speed between two different values v_0 and v_1 can be found by integrating this function with v_0 and v_1 as the bounds.

Averages

The "average" value of the speed of the Maxwell speed distribution.

Most probable speed:

Firstly, by finding the maximum of the MSD (by differentiating, setting the derivative equal to zero and solving for the speed), determine the most probable speed. v_{mp}equation is :

$$v_{\mathrm{mp}} = \left(\frac{2kT}{m}\right)^{1/2}.$$

Root mean square speed:

Second, the root mean square of the speed by finding the expected value of v^2.
(Alternatively, by using the equipartition theorem.) v_{rms}equation is:

$$v_{\mathrm{rms}} = \left(\frac{3kT}{m}\right)^{1/2}.$$

Average speed:

Third and finally, the mean value of *v* from the MSD. $\bar{v}$ equation is:

$$\bar{v} = \left(\frac{8kT}{\pi m}\right)^{1/2}.$$

The equation in the order $v_{\mathrm{mp}} < \bar{v} < v_{\mathrm{rms}}$.

These are three different ways of defining the average velocity, and they are not numerically the same.

Equipartition lawand Limitations of the principle of equipartition of energy.

The equipartition theorem allows the *average*kinetic energy of each atom to be computed, as well as the average potential energies of many vibrational modes.

In classicalstatistical mechanics, the equipartition theorem is a general formula that relates the temperature of a system with its average energies. The equipartition theorem is also known as the law of equipartition, equipartition of energy, or simply equipartition. The original idea of equipartition was that, in thermal equilibrium, energy is shared equally among all of its various forms; for example, the average kinetic energy per degree of freedom in the translational motion of a molecule should equal that of its rotational motions.

The equipartition theorem makes quantitative predictions. It gives the total average kinetic and potential energies for a system at a given temperature, from which the system's heat capacity can be computed. However, equipartition also gives the average values of individual components of the energy, such as the kinetic energy of a particular particle or the potential energy of a single spring. For example, it predicts that every molecule in a monoatomicideal gas has an average kinetic energy of $(3/2)k_BT$ in thermal equilibrium, where k_B is the Boltzmann constant and T is the (thermodynamic) temperature. Generally, it can be applied to any classical system in thermal equilibrium.

The equipartition theorem can be used to derive the ideal gas law, and the Dulong–Petit law for the specific heat capacities of solids.

The equipartition theorem makes very accurate predictions in certain conditions, it becomes inaccurate when quantum effects are significant, such as at low temperatures. When the thermal energy k_BT is smaller than the quantum energy spacing in a particular degree of freedom, the average energy and heat capacity of this degree of freedom are less than the values predicted by equipartition.

The name "equipartition" means "equal division," as derived from the Latin*equi* from the antecedent, æquus ("equal or even"), and partition from the antecedent, *partitionem* ("division, portion"). The original concept of equipartition was that the total kinetic energy of a system is shared equally among all of its independent parts, *on the average*, once the system has reached thermal equilibrium. Equipartition also makes quantitative predictions for these energies. For example, it predicts that every atom of a noble gas, in thermal equilibrium at temperature T, has an average translational kinetic energy of $(3/2)k_BT$, where k_B is the Boltzmann constant. In this example, the kinetic energy is quadratic in the velocity. The equipartition theorem shows that in thermal equilibrium, any degree of freedom (such as a component of the position or velocity of a particle) which appears only quadratically in the energy has an average energy of $\frac{1}{2}k_BT$ and therefore contributes $\frac{1}{2}k_B$ to the system's heat capacity.

The last two equations for the energy of the gas molecules amount to what is called the equipartition principle. The gas that we have used in this description are monoatomic (single atom) and therefore have no internal motions such as rotation or vibration. The only motion that these molecules experience is translation as depicted in the box above. Each gas atom has three degrees of translational freedom, motion along x, y, or z. The average energy then per degree of freedom for the translating atomic gas is 1/2 kT per degree of freedom per gas atom or 1/2 RT per degree of freedom per mole of gas atoms. By the equipartition principle the total energy is equally distributed among the degrees of freedom.

For polyatomic molecules thermal energy will also be distributed among the rotations and vibrations of the molecule. In the same way that translating molecules could move along x, y, or z, so too can each of the atoms in a molecule. Thus molecules have a total of 3N degrees of freedom, where N is the number of atoms in the molecule. Of the total 3N degrees of freedom only 3 will be translations of the whole molecule through space. The remainder are internal degrees of freedom: vibrations and rotations. Non-linear polyatomic molecules have three degrees of rotational freedom while linear polyatomic molecules have only two rotational degrees of freedom. Rotation of a linear molecule along its molecular axis does not consume thermal energy (It's easy to roll a pencil). Each rotation is allotted 1/2 kT per rotation (or 1/2 RT per mole of rotations) according to the equipartition principle. A mole of water molecules (water is a non-linear molecule), for example, has 3 rotations and 3/2 RT of rotational energy according to the equipartition principle. The water rotations are shown below.

Equipartition of energy among vibrations is similar to that for translations and rotations except that thermal energy may go into potential energy, i.e., into the stiffness of the hypothetical spring connecting vibrating atoms, or into kinetic energy, the frequency of the vibration. Each of these vibrational degrees of freedom obtains 1/2 kT according to the equipartition principle or a full kT per vibration per molecule (a full RT per vibration per mole of molecules). Non-linear molecules have 3N - 6 vibrations, while linear molecules have 3N - 5 vibrations. Water, for example, has 3(3) - 6 = 3 vibrations. The vibrations of water are shown below

According to the equipartition principle the total energy of a mole of water vapor is

$U_{total} = U_{trans} + U_{rot} + U_{vib} = 3/2\ RT + 3/2\ RT + 3RT = 6RT.$

It is important to recognize that the equipartition principle is a classical idea that fails to correctly account for the true quantum energies of molecules, with particularly poor applicability to vibrations.

Each of these vibrational degrees of freedom obtains 1/2 kT according to the equipartition principle or a full kT per vibration per molecule.

Maxwell–Boltzmann statistics

Speed distribution can be derived from Maxwell-Boltzmann distribution.

In statistical mechanics, **Maxwell–Boltzmann statistics** describes the statistical distribution of material particles over various energy states in thermal equilibrium, when the temperature is high enough and density is low enough to render quantum effects negligible.

The expected number of particles with energy ε_i for Maxwell–Boltzmann statistics is N_i where:

$$N_i = N\frac{g_i}{e^{(\epsilon_i-\mu)/kT}} = N\frac{g_i e^{-\epsilon_i/kT}}{Z}$$

where:

- N_i is the number of particles in state i
- ε_i is the energy of the i-th state
- g_i is the degeneracy of energy level i, the number of particle's states (excluding the "free particle" state) with energy ε_i
- μ is the chemical potential

- k is Boltzmann's constant
- T is absolute temperature
- N is the total number of particles

$$N = \sum_i N_i$$

- Z is the partition function

$$Z = \sum_i g_i e^{-\epsilon_i/kT}$$

- $e^{(\ldots)}$ is the exponential function

Equivalently, the distribution is sometimes expressed as

$$\frac{N_i}{N} = \frac{1}{e^{(\epsilon_i-\mu)/kT}} = \frac{e^{-\epsilon_i/kT}}{Z}$$

where the index i now specifies a particular state rather than the set of all states with energy ε_i.

Derivation of the Maxwell–Boltzmann distribution and evaluation of alpha and beta

.

The Boltzmann distribution will be derived using the assumption of distinguishable particles.Suppose we have a number of energy levels, labelled by index i , each level having energy ε_i and containing a total of N_i particles. Assuming that there is only one way to put N_i particles into energy level i.

The number of different ways of performing an ordered selection of one object from N objects is obviously N. The number of different ways of selecting 2 objects from N objects, in a particular order, is thus $N(N - 1)$ and that of selecting n objects in a particular order is seen to be $N! / (N - n)!$. The number of ways of selecting 2 objects from N objects without regard to order is $N(N-1)$ divided by the number of ways 2 objects can be ordered, which is 2!. The number of ways of selecting n objects from N objects the order is the binomial coefficient: $N! / n!(N-n)!$. If a set of boxes numbered $1, 2, \ldots, k$, the number of ways of selecting N_1 objects from N objects and placing them in box 1, then selecting N_2 objects from the remaining $N - N_1$ objects and placing them in box 2 etc. is

$$W = \left(\frac{N!}{N_1!(N-N_1)!}\right)\left(\frac{(N-N_1)!}{N_2!(N-N_1-N_2)!}\right)\cdots\left(\frac{N_k!}{N_k!0!}\right)$$
$$= N!\prod_{i=1}^{k}(1/N_i!)$$

where the extended product is over all boxes containing one or more objects. If the i-th box has a "degeneracy" of g_i, that is, it has g_i sub-boxes, such that any way of filling the i-th box where the number in the sub-boxes is changed is a distinct way of filling the box, then the number of ways of filling the i-th box must be increased by the number of ways of distributing the N_i objects in the g_i boxes. The number of ways of placing N_i distinguishable objects in g_i boxes is $g_i^{N_i}$. The number of ways (W) that N atoms can be arranged in energy levels each level i having g_i distinct states such that the i-th level has N_i atoms is:

$$W = N!\prod \frac{g_i^{N_i}}{N_i!}$$

For example, suppose three particles are considered a, b, and c, and we have three energy levels with degeneracies 1, 2, and 1 respectively. There are 6 ways to arrange the 3 particles so that $N_1 = 2$, $N_2 = 1$ and $N_3 = 0$.

. . . . . .

c . . c b . . b a . . a

ab ab ac ac bc bc

The six ways are calculated from the formula:

$$W = N!\prod \frac{g_i^{N_i}}{N_i!} = 3!\left(\frac{1^2}{2!}\right)\left(\frac{2^1}{1!}\right)\left(\frac{1^0}{0!}\right) = 6$$

The set of N_i for which W is maximized, subject to the constraint that there be a fixed number of particles, and a fixed energy. The maxima of W and $\ln(W)$ are achieved by the same values of N_i and, since it is easier to accomplish mathematically, we will maximize the latter function instead. We constrain our solution using Lagrange multipliers forming the function:

$$f(N_1, N_2, \dots, N_n) = \ln(W) + \alpha(N - \sum N_i) + \beta(E - \sum N_i\epsilon_i)$$

Using Stirling's approximation for the factorials

$$N! \approx N^N e^{-N},$$

we obtain:

$$\ln(N!) = N\ln N - N$$

Then

$$\ln W = \ln\left[N!\prod_{i=1}^{n}\frac{g_i^{N_i}}{N_i!}\right] = \ln N! + \sum_{i=1}^{n}(N_i \ln g_i - N_i \ln N_i + N_i)$$

Finally

$$f(N_1, N_2, \dots, N_n) = N\ln(N) - N + \alpha N + \beta E + \sum_{i=1}^{n}(N_i \ln g_i - N_i \ln N_i + N_i - (\alpha - \beta\epsilon_i)N_i)$$

In order to maximize the expression above we apply Fermat's theorem (stationary points), according to which local extrema, if exist, must be at critical points (partial derivatives vanish):

$$\frac{\partial f}{\partial N_i} = \ln g_i - \ln N_i - (\alpha + \beta\epsilon_i) = 0$$

By solving the equations above ($i = 1 \ldots n$) we arrive to an expression for N_i:

$$N_i = \frac{g_i}{e^{\alpha+\beta\epsilon_i}}$$

It can be shown thermodynamicallythat β = 1/*kT* where k is Boltzmann's constant and *T* is the temperature, and that α = -μ/*kT* where μ is the chemical potential, so that finally:

$$N_i = \frac{g_i}{e^{(\epsilon_i-\mu)/kT}}$$

The above formula is sometimes written:

$$N_i = \frac{g_i}{e^{\epsilon_i/kT}/z}$$

where $z = exp(\mu / kT)$ is the absolute activity.

Negative Absolute Temperature :

The equation used

$$\sum_i N_i = N$$

to obtain the population numbers as

$$N_i = N\frac{g_i e^{-\epsilon_i/kT}}{Z}$$

where Z is the partition function defined by:

$$Z = \sum_i g_i e^{-\epsilon_i/kT}$$

- In this formulation, the initial assumption "...*suppose the system has total N particles*..." is dispensed with. Indeed, the number of particles possessed by the system plays no role in arriving at the distribution. Rather, how many particles would occupy states with energy ε_i follows as an easy consequence.
- The presented above is essentially a derivation of the canonical partition function. The Boltzmann sum over states is really no different from the canonical partition function.
- Exactly the same approach can be used to derive Fermi–Dirac and Bose–Einstein statistics. However, there one would replace the canonical ensemble with the grand canonical ensemble, since there is exchange of particles between the system and the reservoir. Also, the system one considers in those cases is a single particle *state*, not a particle. (In the above discussion, we have assumed our system to be a single atom.)

Limits of applicability

The Bose–Einstein and Fermi–Dirac distributions may be written:

$$N_i = \frac{g_i}{e^{(\epsilon_i-\mu)/kT} \pm 1}.$$

Assuming the minimum value of ε_i is small, it can be seen that the condition under which the Maxwell–Boltzmann distribution is valid is when

$$e^{-\mu/kT} \gg 1.$$

For an ideal gas, we can calculate the chemical potential using the development in the Sackur–Tetrode article to show that:

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} = -kT\ln\left(\frac{V}{N\Lambda^3}\right)$$

where E is the total internal energy, S is the entropy, V is the volume, and Λ is the thermal de Broglie wavelength. The condition for the applicability of the Maxwell–Boltzmann distribution for an ideal gas is again shown to be

$$\frac{V}{N\Lambda^3} \gg 1.$$

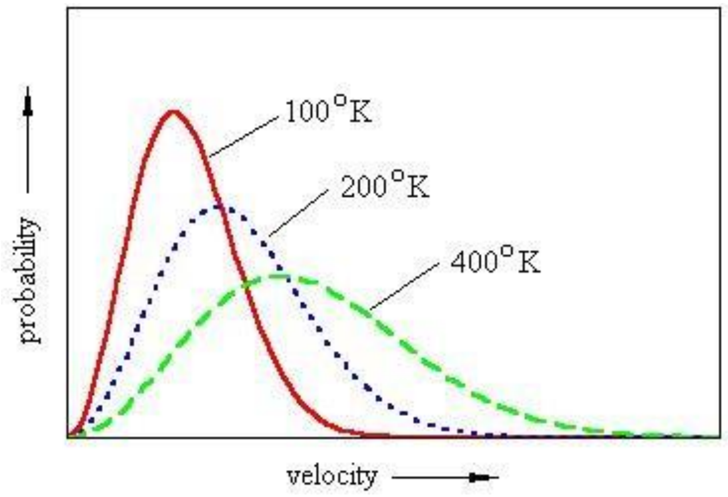
Maxwell-Boltzmann Distribution Law

$$\mathrm{dN} = 4\pi \mathrm{N}\left(\frac{\mathrm{m}}{2\pi \mathrm{kT}}\right)^{\frac{3}{2}} \exp\left(-\frac{\frac{1}{2}\mathrm{mv}^2}{\mathrm{kT}}\right)\mathrm{v}^2\,\mathrm{dv}$$

T is the absolute temperature, N is number of molecules, m is mass of a molecule, v is the velocity of a molecule, k is the Boltzmann constant 13.805 x 10^{-24} J deg^{-1}.

The equation gives the fraction of gas molecules with velocities in the range v to $v + dv$. The velocity is described as a vector with components v_x, v_y and v_z in velocity space. The volume of the spherical shell from surfaces v and $v + dv$ is given by 4□ v^2dv. The transfer of momentum during collisions between molecules, Maxwell determined that the volume element must be multiplied by the Boltzmann factor $exp(-1/2\ mv^2/kT)$. ($1/2mv^2$ as the expression for kinetic energy.) $(m/2kT)^{1/2}$ is a normalization factor required to make the integral of dN over all velocities equal N.

Below is a plot of the probability distribution of molecules as a function of velocity at three temperatures.



Translational Mode

Here we applied quantum mechanics to the particle in a box. The expression for the translational energy of a single gaseous atom, namely,

$$\varepsilon_{tr} = \frac{h^2}{8mV^{2/3}}\left(n_1^2 + n_2^2 + n_3^2\right)$$

where the three spatial quantum numbers, n_1, n_2, and n_3, can each take on any value from unity to infinity. The contribution to thermodynamicproperties from any independent energy mode can be ascertained by first determining itscontribution to the partition function. For the translational mode, the partition functioncan be evaluated most directly by summing over states rather than over levels.

$$Z_{tr} = \sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty} \exp\left[-\frac{h^2}{8mV^{2/3}kT}\left(n_1^2 + n_2^2 + n_3^2\right)\right]$$

For the translational partition function,

$$Z_{tr} = \left\{\sum_{n=1}^{\infty} \exp\left(-\frac{\theta_t n^2}{T}\right)\right\}^3 \quad (1)$$

For the characteristic translational temperature,

$$\theta_t = \frac{h^2}{8mkV^{2/3}} \quad (2)$$

The summation of above Equation is identical for the three translational quantum numbers. Moreover, by summing over all possible values from unity to infinity, we are indeed accounting for each quantum state, as identified by its unique set of translational quantum numbers.

Recall that $\theta t \approx 10-16$ K; thus, for any realistic assembly temperature,the summation in the above Eq. can be converted to an equivalent integration. In other words, because of the incredibly minute separation between consecutivetranslational levels, we may assume a continuous distribution of translational energies, asmight be expected from classical mechanics. Consequently, from Eq. (1)becomes

$$Z_{tr} = \left\{ \int_0^\infty \exp\left(-\frac{\theta_t n^2}{T}\right) dn \right\}^3 = \left\{ \frac{1}{2}\sqrt{\frac{\pi T}{\theta_t}} \right\}^3 \tag{3}$$

so that, substituting Eq. (2) into Eq. (3), we obtain

$$Z_{tr} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V \tag{4}$$

The *translational partition function*, as defined by Eq. (4), can also be derived by either (1) summing over energy levels using the density of states or (2) evaluating the phase integral. For quantum mechanics is actually unnecessary for the translational energymode; hence, the equipartition principle is perfectly suitable for calculating translationalcontributions to thermodynamic properties.

Because the characteristic temperature for the translational mode is so much smaller than that for the various internal energy modes, the total number of quantum states for an atom or molecule is essentially equivalent to that for the translational mode.

$$\frac{Z}{N} \simeq \frac{Z_{tr}}{N} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \left(\frac{V}{N}\right) \gg 1 \tag{5}$$

For an ideal gas at its standard temperature and pressure of 298.15 K and 1 bar, Eq. (5) typically gives Ztr/N 10^5, which certainly supports the dilute limit. Dilute conditions may not exist at low temperaturesor high densities, especially for particles with nearly zero mass.

Employing the translational partition function, we may now evaluate the contributions of the translational mode to the thermodynamic properties of an ideal gas. Considering, for example, the internal energy,

$$\left(\frac{u}{RT}\right)_{tr} = T\left(\frac{\partial \ln Z_{tr}}{\partial T}\right)_V = \frac{3}{2} \quad (6)$$

Similarly, for the specific heat at constant volume,

$$\left(\frac{c_v}{R}\right)_{tr} = \left[\frac{\partial}{\partial T}T^2\left(\frac{\partial \ln Z_{tr}}{\partial T}\right)\right]_V = \frac{3}{2} \quad (7)$$

Therefore, the translational contribution to the internal energy per mole is 1.5RT and that to the heat capacity per mole is 1.5R, which is in perfect accord with our expectations from the equipartition principle. The translational contributions to the specific enthalpy andspecific heat at constant pressure are as follows:

$$\left(\frac{h}{RT}\right)_{tr} = \frac{5}{2} \qquad \left(\frac{c_p}{R}\right)_{tr} = \frac{5}{2}$$

At this point, the pressure can be easily determined by combining aspects of classical and statistical thermodynamics. In particular, the pressure can be expressed classically as

$$-P = \left(\frac{\partial A}{\partial V}\right)_{T,N} \quad (8)$$

while the Helmholtz free energy,

$$A = -NkT\left[\ln\left(\frac{Z}{N}\right) + 1\right]$$

Recalling that $Z = Z(T, V)$, we thus obtain the general relation

$$P = NkT\left(\frac{\partial \ln Z}{\partial V}\right)_T. \quad (9)$$

Applying Eq. (9) to the translational mode, we then obtain, by substitution from Eq. (4),

$$PV = NkT \quad (10)$$

which is, the equation of state for an ideal gas. The pressure arises solely from the translational mode, as surely expected from the momentum exchange occurring at all walls for vessels containing independent gaseous particles. On this basis, the partition function for each internal energy mode must depend solely on temperature.

For the entropy,

$$\left(\frac{s}{R}\right)_{tr} = \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + \ln\left(\frac{V}{N}\right) + \frac{5}{2}$$

which becomes, after substitution from Eq. (10),

$$\left(\frac{s}{R}\right)_{tr} = \ln\left[\frac{(2\pi m)^{3/2}(kT)^{5/2}}{h^3 P}\right] + \frac{5}{2} \qquad (11)$$

The *Sackur–Tetrode equation* for translational entropy:

$$\left(\frac{s}{R}\right)_{tr} = \frac{5}{2}\ln T + \frac{3}{2}\ln M - \ln P - 1.1516 \qquad (12)$$

where T is the temperature (K), M is the molecular weight (kg/kmol), and P is the pressure

(bar). Based on Eq. (5), the Sackur–Tetrode equation, which holds only in the dilute limit, is obviously inappropriate for temperatures approaching absolute zero. Hence,the Eq. (12) gives an entropy value of negative infinity at $T = 0$.

Translational energy and ideal gases

The (Newtonian) kinetic energy of a particle of mass m, velocity $\mathbf{v}$ is given by

$$H_{\text{kin}} = \tfrac{1}{2}m|\mathbf{v}|^2 = \tfrac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right),$$

where v_x, v_y and v_z are the Cartesian components of the velocity $\mathbf{v}$. Here, H is short for Hamiltonian, and used as a symbol for energy because the Hamiltonian formalism plays a central role in the most general form of the equipartition theorem.

Since the kinetic energy is quadratic in the components of the velocity, by equipartition these three components each contribute $\frac{1}{2}k_BT$ to the average kinetic energy in thermal equilibrium. Thus the average kinetic energy of the particle is $(3/2)k_BT$, as in the example of noble gases above.

More generally, in an ideal gas, the total energy consists purely of (translational) kinetic energy: by assumption, the particles have no internal degrees of freedom and move independently of one another. Equipartition therefore predicts that the average total energy of an ideal gas of N particles is (3/2) $N_A k_B T$.

The heat capacity of the gas is (3/2) $N_A k_B$, the heat capacity of a mole of such gas particles is (3/2)$N_A k_B$ = (3/2)R, where N_A is the Avogadro constant and R is the gas constant. Since $R \approx 2$ cal/(mol·K), equipartition predicts that the molar heat capacity of an ideal gas is roughly 3 cal/(mol·K).

The mean kinetic energy allows the root mean square speedv_{rms} of the gas particles to be calculated:

$$v_{\mathrm{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}},$$

where $M = N_A m$ is the mass of a mole of gas particles.

Rotational energy

A rotating molecule with principal moments of inertiaI_1, I_2 and I_3. The rotational energy of such a molecule is given by

$$H_{\mathrm{rot}} = \tfrac{1}{2}(I_1\omega_1^2 + I_2\omega_2^2 + I_3\omega_3^2),$$

where ω_1, ω_2, and ω_3 are the principal components of the angular velocity. The equipartition implies that in thermal equilibrium the average rotational energy of each particle is (3/2)$k_B T$. Similarly, the equipartition theorem allows the average (the root mean square) angular speed of the molecules to be calculated.

Rotational Mode

The energy levels and degeneracies for the rigid rotor are given by

$$\tilde{\varepsilon}_{rot} = \frac{\varepsilon_{rot}}{hc} = J(J+1)B_e \qquad g_J = 2J+1 \tag{1}$$

so that the rotational partition function becomes

$$Z_{rot} = \sum_J g_J e^{-\varepsilon_J/kT} = \sum_{J=0}^{\infty} (2J+1)\exp[-J(J+1)\theta_r/T] \qquad (2)$$

Here, the characteristic rotational temperature,

$$\theta_r = \frac{hc}{k} B_e = \frac{h^2}{8\pi^2 k I_e}, \quad (3)$$

for which the moment of inertia $Ie = \mu r^2 e$. Unfortunately, for a homonuclear diatomic such

as O_2 or N_2, we have inadvertently overcounted the number of available quantum states by a factor of two because of the inherent indistinguishability of the nuclear pair.

From symmetry requirements on the molecular wave function, as generated by the usual coupling between nuclear spin and orbital rotation. As a result,the partition function is restricted to only odd or even values of the rotational quantum number.

The *rotational partition function* can be expressed more generally as

$$Z_{rot} = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1)\exp[-J(J+1)\theta_r/T] \qquad (4)$$

where σ is a *symmetry factor*, which, by definition, takes values of unity for a heteronuclear

and two for a homonuclear diatomic molecule.

Typically, $\theta r < T$, using a standard Euler–Maclaurin expansion

$$Z_{rot} = \frac{T}{\sigma\theta_r}\left[1 + \frac{1}{3}\left(\frac{\theta_r}{T}\right) + \frac{1}{15}\left(\frac{\theta_r}{T}\right)^2 + \frac{4}{315}\left(\frac{\theta_r}{T}\right)^3 + \cdots\right] \qquad (5)$$

If, on the other hand, θr -T, the summation in Eq. (4) can be converted to an integration,as for our evaluation of the translational partition function. The obvious result fromEq. (5) is

$$Z_{rot} = \frac{T}{\sigma\theta_r} \qquad (6)$$

Now, for nearly all diatomics, θr^2 K, so that Eq. (6) is perfectly suitable for most computations. However, for molecules containing a hydrogen atom, such as HCl or OH, θr15 K; thus, for such cases, Eq. (5) becomes necessary. In contrast, direct summation via Eq. (4) remains a requirement for H_2, as here θr = 87.55 K. With Eq. (3) calculating the rotational partition function for lighter molecules.

Eq. (6) controls so that our two standard partial derivatives for the partition functionwith respect to temperature become

$$T\left(\frac{\partial \ln Z_{rot}}{\partial T}\right)_V = 1 \qquad \left[\frac{\partial}{\partial T}T^2\left(\frac{\partial \ln Z_{rot}}{\partial T}\right)\right]_V = 1$$

Therefore, as for the translational mode, we again replicate the classical results predicted by the equipartition principle:

$$\left(\frac{u}{RT}\right)_{rot} = \left(\frac{h}{RT}\right)_{rot} = 1 \quad (7)$$

$$\left(\frac{c_v}{R}\right)_{rot} = \left(\frac{c_p}{R}\right)_{rot} = 1 \quad (8)$$

For the rotational contribution to the entropy,

$$\left(\frac{s}{R}\right)_{rot} = 1 + \ln\left(\frac{T}{\sigma\theta_r}\right) \quad (9)$$

For heteronuclear diatomics containing atomic hydrogen, $3 < T/\theta r \leq 30$, which implies utilization of Eq. (5); for this case, the rotational partition function can be expressed as

$$Z_{rot} = \frac{T}{\sigma\theta_r} Z_{rc}$$

where we have defined the rotational correction term,

$$Z_{rc} = 1 + \frac{1}{3}\left(\frac{\theta_r}{T}\right) + \frac{1}{15}\left(\frac{\theta_r}{T}\right)^2 + \frac{4}{315}\left(\frac{\theta_r}{T}\right)^3 + \cdots \quad (10)$$

Evaluating two standard partial derivatives, term-by-term, we find algebraic manipulation,

$$T\left(\frac{\partial \ln Z_{rot}}{\partial T}\right)_V = 1 - \frac{Z'_{rc}}{Z_{rc}}$$ (11)

$$\left[\frac{\partial}{\partial T}T^2\left(\frac{\partial \ln Z_{rot}}{\partial T}\right)\right]_V = 1 + \frac{Z''_{rc} - Z'_{rc}}{Z_{rc}} - \left(\frac{Z'_{rc}}{Z_{rc}}\right)^2$$ (12)

$$Z'_{rc} = \frac{1}{3}\left(\frac{\theta_r}{T}\right) + \frac{2}{15}\left(\frac{\theta_r}{T}\right)^2 + \frac{12}{315}\left(\frac{\theta_r}{T}\right)^3 + \cdots$$ (13)

$$Z''_{rc} = \frac{1}{3}\left(\frac{\theta_r}{T}\right) + \frac{4}{15}\left(\frac{\theta_r}{T}\right)^2 + \frac{36}{315}\left(\frac{\theta_r}{T}\right)^3 + \cdots$$ (1 4)

Hence, from Eqs. (11) and (12), we have for the rotational contributions to the internal energy, enthalpy, and specific heats

$$\left(\frac{u}{RT}\right)_{rot} = \left(\frac{h}{RT}\right)_{rot} = 1 - \frac{Z'_{rc}}{Z_{rc}}$$ (15)

$$\left(\frac{c_v}{R}\right)_{rot} = \left(\frac{c_p}{R}\right)_{rot} = 1 + \frac{Z''_{rc} - Z'_{rc}}{Z_{rc}} - \left(\frac{Z'_{rc}}{Z_{rc}}\right)^2$$ (16)

Similar expressions could be developed for all of the remaining thermodynamic properties,
including the entropy.
Consider a heteronucleardiatomic with a molecular distribution given,

$$\frac{N_J}{N} = \frac{g_J e^{-\varepsilon_J/kT}}{Z_{rot}} = \frac{(2J+1)}{Z_{rot}}\exp\left[-\frac{J(J+1)\theta_r}{T}\right]$$ (17)

Dividing Eq. (17) by its result at $J = 0$, we obtain

$$\frac{N_J}{N_0} = (2J+1)\exp\left[-\frac{J(J+1)\theta_r}{T}\right]$$ (18)

For $T/\theta r = 100$, accents the remarkablepeak that typically arises at a rotational quantum number $J > 0$. Based on our discussion inwe would normally expect the population to peak at its ground level, with anexponentially decreasing population at higher levels.The rotational case demonstrates that a strongly increasing degeneracy with risingenergy level can preferentially displace the maximum population away from its ground level.For atoms having low-lyingelectronic levels with degeneracies significantly greater than that for the ground electronicstate. Assuming, for the moment, a continuous rather than a discrete distribution, determine from Eq. (18) that value of the rotational quantum number corresponding tothe peak in the rotational distribution, which becomes

$$J_{max} = \sqrt{\frac{T}{2\theta_r}} - \frac{1}{2} \qquad (19)$$

For the rotationaldistribution can be very important for many optical techniques used to determine theconcentration or temperature in a gaseous mixture. In particular, the rotational peakusually offers the most intense signal in a rovibronic spectrum, and thus the best possibledetection limit.

Potential energy and harmonic oscillators

Equipartition applies to potential energies as well as kinetic energies: important examples include harmonic oscillators such as a spring, which has a quadratic potential energy

$$H_{\text{pot}} = \tfrac{1}{2}aq^2,$$

where the constant a describes the stiffness of the spring and q is the deviation from equilibrium. If such a one dimensional system has mass m, then its kinetic energy H_{kin} is

$$H_{\text{kin}} = \frac{1}{2}mv^2 = \frac{p^2}{2m},$$

where v and $p = mv$ denote the velocity and momentum of the oscillator. Combining these terms yields the total energy.

$$H = H_{\text{kin}} + H_{\text{pot}} = \frac{p^2}{2m} + \frac{1}{2}aq^2.$$

Equipartition therefore implies that in thermal equilibrium, the oscillator has average energy

$$\langle H\rangle = \langle H_{\text{kin}}\rangle + \langle H_{\text{pot}}\rangle = \tfrac{1}{2}k_B T + \tfrac{1}{2}k_B T = k_B T,$$

where the angular brackets $\langle \cdots \rangle$ denote the average of the enclosed quantity.

This result is valid for any type of harmonic oscillator, such as a pendulum, a vibrating molecule or a passive electronic oscillator. Systems of such oscillators arise in many situations; by equipartition, each such oscillator receives an average total energy k_BT and hence contributes k_B to the system's heat capacity. Atoms in a crystal can vibrate about their equilibrium positions in the lattice. Such vibrations account largely for the heat capacity of crystalline dielectrics; with metals, electrons also contribute to the heat capacity.

Specific heat capacity of solids

An important application of the equipartition theorem is to the specific heat capacity of a crystalline solid. Each atom in such a solid can oscillate in three independent directions, so the solid can be viewed as a system of $3N$ independent simple harmonic oscillators, where N denotes the number of atoms in the lattice. Since each harmonic oscillator has average energy k_BT, the average total energy of the solid is $3Nk_BT$, and its heat capacity is $3Nk_B$.

By taking N to be the Avogadro constant N_A, and using the relation $R = N_Ak_B$ between the gas constant R and the Boltzmann constant k_B, this provides an explanation for the Dulong–Petit law of specific heat capacities of solids, which stated that the specific heat capacity (per unit mass) of a solid element is inversely proportional to its atomic weight. A modern version is that the molar heat capacity of a solid is $3R \approx 6$ cal/(mol·K).

However, this law is inaccurate at lower temperatures, due to quantum effects; it is also inconsistent with the experimentally derived third law of thermodynamics, according to which the molar heat capacity of any substance must go to zero as the temperature goes to absolute zero. The motions of oscillators can be decomposed into normal modes, like the vibrational modes of a piano string or the resonances of an organ pipe. On the other hand, equipartition often breaks down for such systems, because there is no exchange of energy between the normal modes. In an extreme situation, the modes are independent and so their energies are independently conserved.

Boltzmann applied the equipartition theorem to provide a theoretical explanation of the Dulong–Petit law for the specific heat capacities of solids.

The molar specific heat of a diatomic gas against temperature. It agrees with the value (7/2)*R* predicted by equipartition at high temperatures (where *R* is the gas constant), but decreases to (5/2)*R* and then (3/2)*R* at lower temperatures, as the vibrational and rotational modes of motion are "frozen out".

The failure of the equipartition theorem led to a paradox that was only resolved by quantum mechanics. For most molecules, the transitional temperature T_{rot} is much less than room temperature, whereas T_{vib} can be ten times larger or more. A typical example is carbon monoxide, CO, for which $T_{rot} \approx 2.8$ K and $T_{vib} \approx 3103$ K. For molecules with very large or weakly bound atoms, T_{vib} can be close to room temperature (about 300 K); for example, $T_{vib} \approx 308$ K for iodine gas, I_2.

Einstein used the failure of equipartition to argue for the need of a new quantum theory of matter.

Applications

Ideal gas law

Ideal gases provide an important application of the equipartition theorem

$$\begin{aligned}\langle H^{\mathrm{kin}}\rangle &= \frac{1}{2m}\langle p_x^2 + p_y^2 + p_z^2\rangle \\ &= \frac{1}{2}\left(\left\langle p_x \frac{\partial H^{\mathrm{kin}}}{\partial p_x}\right\rangle + \left\langle p_y \frac{\partial H^{\mathrm{kin}}}{\partial p_y}\right\rangle + \left\langle p_z \frac{\partial H^{\mathrm{kin}}}{\partial p_z}\right\rangle\right) = \frac{3}{2}k_B T\end{aligned}$$

for the average kinetic energy per particle, the equipartition theorem can be used to derive the ideal gas law from classical mechanics. If **q** = (q_x, q_y, q_z) and **p** = (p_x, p_y, p_z) denote the position vector and momentum of a particle in the gas, and **F** is the net force on that particle, then

$$\begin{aligned}\langle \mathbf{q}\cdot\mathbf{F}\rangle &= \left\langle q_x \frac{dp_x}{dt}\right\rangle + \left\langle q_y \frac{dp_y}{dt}\right\rangle + \left\langle q_z \frac{dp_z}{dt}\right\rangle \\ &= -\left\langle q_x \frac{\partial H}{\partial q_x}\right\rangle - \left\langle q_y \frac{\partial H}{\partial q_y}\right\rangle - \left\langle q_z \frac{\partial H}{\partial q_z}\right\rangle = -3k_B T,\end{aligned}$$

where the first equality is Newton's second law, and the second line uses Hamilton's equations and the equipartition formula. Summing over a system of N particles yields

$$3Nk_BT = -\left\langle \sum_{k=1}^{N} \mathbf{q}_k \cdot \mathbf{F}_k \right\rangle.$$

The kinetic energy of a particular molecule can fluctuate, but the equipartition theorem allows its *average* energy to be calculated at any temperature. Equipartition also provides a derivation of the ideal gas law, an equation that relates the pressure, volume and temperature of the gas.

By Newton's third law and the ideal gas assumption, the net force on the system is the force applied by the walls of their container, and this force is given by the pressure P of the gas. Hence

$$-\left\langle \sum_{k=1}^{N} \mathbf{q}_k \cdot \mathbf{F}_k \right\rangle = P \oint_{\mathrm{surface}} \mathbf{q}\cdot \mathbf{dS},$$

where **d*S*** is the infinitesimal area element along the walls of the container. Since the divergence of the position vector **q** is

$$\boldsymbol{\nabla}\cdot\mathbf{q} = \frac{\partial q_x}{\partial q_x} + \frac{\partial q_y}{\partial q_y} + \frac{\partial q_z}{\partial q_z} = 3,$$

the divergence theorem implies that

$$P \oint_{\mathrm{surface}} \mathbf{q} \cdot \mathbf{dS} = P \int_{\mathrm{volume}} \left(\boldsymbol{\nabla} \cdot \mathbf{q} \right) dV = 3PV,$$

where dV is an infinitesimal volume within the container and V is the total volume of the container.

Putting these equalities together yields

$$3Nk_BT = -\left\langle \sum_{k=1}^{N} \mathbf{q}_k \cdot \mathbf{F}_k \right\rangle = 3PV,$$

which immediately implies the ideal gas law for N particles:

$$PV = Nk_BT = nRT,$$

where $n = N/N_A$ is the number of moles of gas and $R = N_Ak_B$ is the gas constant. The equipartition provides a simple derivation of the ideal-gas law and the internal energy, the same results can be obtained by an alternative method using the partition function.

Diatomic gases

A diatomic gas can be modelled as two masses, m_1 and m_2, joined by a spring of stiffness$a$, which is called the *rigid rotor-harmonic oscillator approximation*. The classical energy of this system is

$$H = \frac{\left|\mathbf{p}_1\right|^2}{2m_1} + \frac{\left|\mathbf{p}_2\right|^2}{2m_2} + \frac{1}{2}aq^2,$$

where $\mathbf{p}_1$ and $\mathbf{p}_2$ are the momenta of the two atoms, and q is the deviation of the inter-atomic separation from its equilibrium value. Every degree of freedom in the energy is quadratic and, thus, should contribute $\frac{1}{2}k_BT$ to the total average energy, and $\frac{1}{2}k_B$ to the heat capacity. Therefore, the heat capacity of a gas of N diatomic molecules is predicted to be $7N\cdot\frac{1}{2}k_B$: the momenta $\mathbf{p}_1$ and $\mathbf{p}_2$ contribute three degrees of freedom each, and the extension q contributes the seventh. It follows that the heat capacity of a mole of diatomic molecules with no other degrees of freedom should be $(7/2)N_Ak_B = (7/2)R$ and, thus, the predicted molar heat capacity should be roughly 7 cal/(mol·K). However, the experimental values for molar heat capacities of diatomic gases are typically about 5 cal/(mol·K) and fall to 3 cal/(mol·K) at very low temperatures. This disagreement between the equipartition prediction and the experimental value of the molar heat capacity cannot be explained by using a more complex model of the molecule, since adding more degrees of freedom can only *increase* the predicted specific heat, not decrease it.

Relativistic ideal gases

Equipartition was used above to derive the classical ideal gas law from Newtonian mechanics. However, relativistic effects become dominant in some systems, such as white dwarfs and neutron stars, and the ideal gas equations must be modified. The equipartition theorem provides a convenient way to derive the corresponding laws for an extreme relativistic ideal gas. In such cases, the kinetic energy of a single particle is given by the formula

$$H_{\mathrm{kin}} \approx cp = c\sqrt{p_x^2 + p_y^2 + p_z^2}.$$

Taking the derivative of H with respect to the p_x momentum component gives the formula

$$p_x \frac{\partial H_{\mathrm{kin}}}{\partial p_x} = c\frac{p_x^2}{\sqrt{p_x^2 + p_y^2 + p_z^2}}$$

and similarly for the p_y and p_z components. Adding the three components together gives

$$\begin{aligned}\langle H_{\mathrm{kin}}\rangle &= \left\langle c\frac{p_x^2+p_y^2+p_z^2}{\sqrt{p_x^2+p_y^2+p_z^2}}\right\rangle \\ &= \left\langle p_x\frac{\partial H^{\mathrm{kin}}}{\partial p_x}\right\rangle + \left\langle p_y\frac{\partial H^{\mathrm{kin}}}{\partial p_y}\right\rangle + \left\langle p_z\frac{\partial H^{\mathrm{kin}}}{\partial p_z}\right\rangle \\ &= 3k_BT\end{aligned}$$

where the last equality follows from the equipartition formula. Thus, the average total energy of an extreme relativistic gas is twice that of the non-relativistic case: for N particles, it is 3 Nk_BT.

Non-ideal gases

In an ideal gas the particles are assumed to interact only through collisions. The equipartition theorem may also be used to derive the energy and pressure of "non-ideal gases" in which the particles also interact with one another through conservative forces whose potential $U(r)$ depends only on the distance r between the particles. A single gas particle, and approximating the rest of the gas by a spherically symmetric distribution. Aradial distribution function$g(r)$ such that the probability density of finding another particle at a distance r from the given particle is equal to $4\pi r^2\rho g(r)$, where $\rho = N/V$ is the mean density of the gas. It follows the mean potential energy associated to the interaction of the given particle with the rest of the gas is

$$\langle h_{\mathrm{pot}}\rangle = \int_0^\infty 4\pi r^2 \rho U(r) g(r)\, dr.$$

The total mean potential energy of the gas is therefore $\langle H_{pot}\rangle = \frac{1}{2}N\langle h_{\mathrm{pot}}\rangle$, where N is the number of particles in the gas, and the factor ½ is needed because summation over all the particles counts each interaction twice. Adding kinetic and potential energies, then applying equipartition, yields the *energy equation*

$$H = \langle H_{\mathrm{kin}}\rangle + \langle H_{\mathrm{pot}}\rangle = \frac{3}{2}Nk_BT + 2\pi N\rho\int_0^\infty r^2 U(r) g(r)\, dr.$$

To derive the *pressure equation*

$$3Nk_\mathrm{B}T = 3PV + 2\pi N\rho \int_0^\infty r^3 U'(r) g(r)\, dr.$$

Kinetic energies and the Maxwell–Boltzmann distribution

The equipartition theorem states that, in any physical system in thermal equilibrium, every particle has exactly the same average kinetic energy, $(3/2)k_\mathrm{B}T$. The Maxwell–Boltzmann distribution which is the probability distribution

$$f(v) = 4\pi \left(\frac{m}{2\pi k_\mathrm{B}T} \right)^{3/2} v^2 \exp\left(\frac{-mv^2}{2k_\mathrm{B}T} \right)$$

for the speed of a particle of mass m in the system, where the speed v is the magnitude $\sqrt{v_x^2 + v_y^2 + v_z^2}$ of the velocityvector

$$\mathbf{v} = (v_x, v_y, v_z).$$

The Maxwell–Boltzmann distribution applies to any system composed of atoms, and assumes only a canonical ensemble, specifically, that the kinetic energies are distributed according to their Boltzmann factor at a temperature T. The average kinetic energy for a particle of mass m is then given by the integral formula

$$\langle H_\mathrm{kin} \rangle = \langle \tfrac{1}{2}mv^2 \rangle = \int_0^\infty \tfrac{1}{2}mv^2\ f(v)\ dv = \tfrac{3}{2}k_\mathrm{B}T,$$

as stated by the equipartition theorem. The same result can also be obtained by averaging the particle energy using the probability of finding the particle in certain quantum energy state.

Quadratic energies and the partition function

More generally, the equipartition theorem states that any degree of freedom$x$ which appears in the total energy H only as a simple quadratic term Ax^2, where A is a constant, has an average energy of ½$k_B T$ in thermal equilibrium. In this case the equipartition theorem may be derived from the partition function$Z(\beta)$, where $\beta = 1/(k_B T)$ is the canonical inverse temperature. Integration over the variable x yields a factor

$$Z_x = \int_{-\infty}^{\infty} dx\ e^{-\beta A x^2} = \sqrt{\frac{\pi}{\beta A}},$$

in the formula for Z. The mean energy associated with this factor is given by

$$\langle H_x \rangle = -\frac{\partial \log Z_x}{\partial \beta} = \frac{1}{2\beta} = \frac{1}{2} k_B T$$

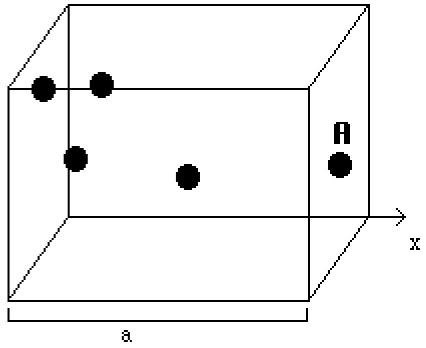
as stated by the equipartition theorem.

Kinetic Molecular Theory of Gases

Kinetic Molecular Theory of Gases

The volume of a gas increases with temperature. The velocity (or kinetic energy) of gas molecules increases at the temperatures increases. Determine the connection between temperature and the velocity of gases by the molecular dynamics of a gas which produce a pressure inside a container.

The volume of the box is a x A where a is the size of the box along the x-axis and A is the area of the wall of the box that is perpendicular to the x-axis.



Pressure is defined as the force per unit area.

$$\text{pressure} = \frac{force}{area}$$

To calculate the pressure need to determine the force exerted by gas molecules colliding with wall A. The force exerted by a molecule of mass m colliding with wall A can be calculated from

$$\text{force} = \text{mass x acceleration} = \text{mass x} \frac{\Delta\ \text{velocity}}{\Delta\ \text{time}}.$$

The last quantity in the above equation can be determined if we know the change in velocity per collision with wall A and the time between collisions with wall A. A collision with wall A will reverse only the x-component of the velocity . If we assign the average initial x-component of the velocity before collision as $-v_x$ and the final x-component of the velocity after collision to v_x then the change in velocity with collision with wall A is

$$\Delta\ \text{velocity} = v_x - (-v_x) = 2\ v_x$$

The time between collisions with wall A will again depend upon the x-component of the velocity and the distance travelled by the gas molecule (along x) between collisions. In our box a gas molecule, after colliding with wall A, would have to travel along x to the opposite wall, a distance of a, and back again to wall A, for a total distance travelled along x of 2a. Thus the time between collisions with wall A would be

$$\Delta \text{ time} = \frac{2a}{v_x}$$

and the force exerted by one gas molecule of mass m colliding with wall A becomes

$$\text{force} = m \times \frac{2v_x}{\left(\frac{2a}{v_x}\right)} = \frac{mv_x^2}{a}$$

and the pressure at wall A becomes

$$\text{pressure} = \frac{\text{force}}{\text{area}} = \frac{mv_x^2}{aA} = \frac{mv_x^2}{V} \doteq p$$

Rearranging we find

$pV = mv_x^2$ per gas molecule.

Recognizing that the velocity is related to its components by the Pythagorean Theorem and that, on average, each of the components are equal we find:

$v^2 = v_x^2 + v_y^2 + v_z^2 = 3v_x^2$

and

$pV = 1/3\ mv^2$ per gas molecule,

or

$pV_m = 1/3\ N_A mv^2$ per mole of gas molecules,

where V_m is the volume occupied by a mole of gas molecules and N_A is Avogadro's number (6.022×10^{23} molecules per mole).

From the ideal gas temperature scale, i.e., $pV_m = RT$, finally connect the velocity and kinetic energy of the gas molecules to the temperature.

$pV_m = 1/3\ N_A mv^2 = RT$ and

$$v^2 = \frac{3RT}{N_A m} = \frac{3kT}{m} \quad \text{or} \quad v = \sqrt{\frac{3kT}{m}}$$

and the average kinetic energy (U) of a gas molecule is

$$U = \frac{1}{2} mv^2 = \frac{3}{2} pV = \frac{3}{2} kT$$

and the average kinetic energy ($\overline{U}$) of a mole of gas molecules is

$$\overline{U} = N_A \frac{1}{2} mv^2 = N_A \frac{3}{2} kT = \frac{3}{2} RT.$$

The velocity, v, is the root mean square velocity. At room temperature (300 K) the velocity of nitrogen molecules ($m = 4.65 \times 10^{-26}$ kg) is 519 meters/second. (*Note: k is called Boltzmann's constant and is related to the gas constant R such that $k = R/N_A = 1.38 \times 10^{-23}$ joule per Kelvin per molecule.)

The last two equations for the energy of the gas molecules amount to what is called the *equipartition principle*. The gas that we have used in this description are monoatomic (single atom) and therefore have no internal motions such as rotation or vibration. The only motion that these molecules experience is translation as depicted in the box above. Each gas atom has three degrees of translational freedom, motion along x, y, or z. The average energy then per degree of freedom for the translating atomic gas is 1/2 kT per degree of freedom per gas atom or 1/2 RT per degree of freedom per mole of gas atoms. By the *equipartition principle* the total energy is equally distributed among the degrees of freedom.

For polyatomic molecules thermal energy will also be distributed among the rotations and vibrations of the molecule. In the same way that translating molecules could move along x, y, or z, so too can each of the atoms in a molecule. Thus molecules have a total of 3N degrees of freedom, where N is the number of atoms in the molecule. Of the total 3N degrees of freedom only 3 will be translations of the whole molecule through space. The remainder are internal degrees of freedom: vibrations and rotations. Non-linear polyatomic molecules have three degrees of rotational freedom while linear polyatomic molecules have only two rotational degrees of freedom. Rotation of a linear molecule along its molecular axis does not consume thermal energy (It's easy to roll a pencil). Each rotation is allotted 1/2 kT per rotation (or 1/2 RT per mole of rotations) according to the *equipartition principle.* A mole of water molecules (water is a non-linear molecule), for example, has 3 rotations and 3/2 RT of rotational energy according to the *equipartition principle*. The water rotations are shown below.

Equipartition of energy among vibrations is similar to that for translations and rotations except that thermal energy may go into potential energy, i.e., into the stiffness of the hypothetical spring connecting vibrating atoms, or into kinetic energy, the frequency of the vibration. Each of these vibrational degrees of freedom obtains 1/2 kT according to the *equipartition principle* or a full kT per vibration per molecule (a full RT per vibration per mole of molecules). Non-linear molecules have 3N - 6 vibrations, while linear molecules have 3N - 5 vibrations. Water, for example, has 3(3) - 6 = 3 vibrations. The vibrations of water are shown below

According to the *equipartition principle* the total energy of a mole of water vapor is

$U_{total} = U_{trans} + U_{rot} + U_{vib}$ = 3/2 RT + 3/2 RT + 3RT = 6RT.

It is important to recognize that the *equipartition principle* is a classical idea that fails to correctly account for the true quantum energies of molecules, with particularly poor applicability to vibrations.

Each of these vibrational degrees of freedom obtains 1/2 kT according to the *equipartition principle* or a full kT per vibration per molecule.

	Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answers
1	The partition function is given by the equation __________	$q = \sum g_{i.}\ e^{-\varepsilon i} /kT$	$q =\sum g_i e^{\varepsilon i} /kT$	$q =\sum e^{\varepsilon i} /kT$	$q =\sum e^{-\varepsilon i} /kT$	$q = \sum g_{i.}\ e^{-\varepsilon i} /kT$
2	Canonical Ensemble defined as a collection of a large number of independent assemblies having _____	same temperature , volume and number of identical systems	different temperature , volume and number of identical systems	different volume and same identical systems	different temperature	same temperature , volume and number of identical systems
3	Grand .Canonical Ensemble defined as a collection of a large number of independent assemblies having _______	same temperature , volume and number of identical systems	Same temperature , volume and chemical potential	different temperature , volume and number of identical systems	different temperature only	Same temperature , volume and chemical potential
4	The total partition function equation is _________	$q =q_{tr}.q_{rot}.q_{vib}..q_{ele}$	$q =q_{tr}.q_{ele}$	$q =q_{tr}.q_{vib}$	$q = q_{rot}.q_{vib}$	$q =q_{tr}.q_{rot}.q_{vib}..q_{ele}$
5	The units of molecular partition function are _________	cm^{-1}	s^{-1}	$JK^{-1}mol^{-1}$	dimensionless	dimensionless
6	If Q is the molar (canonical) partition function ,then the work function A, is given by	A=kT ln Q	A= -kT ln Q	A=lnQ/kT	A=kT/lnQ	A= -kT ln Q

7	In terms of the molecular partition function q, the internal energy of a molecule is given by	$U=nRT^2(dlnq/dv)T$	$U=nRT(dlnq/dv)T$	$U=nRT^2(dlnq/dT)v$	$U=nRT(dlnq/dv)$ T	$U=nRT^2(dlnq/dT)v$
8	Which of the following is true	$q=q_{tr}xq_{rot} +q_{vib}xq_{ele}$	$q=q_{tr}xq_{rot}xq_{vib}xq_{ele}$	$q=(q_{tr}+q_{rot})(q_{vib}+q_{ele})$	$q=(q_{tr}xq_{rot})/(q_{vib}/ q_{ele})$	$q=q_{tr}xq_{rot}xq_{vib}xq_{ele}$
9	The zero-point energy of an S.H.O. whose vibrational frequency is v, is given by ____________	hv	hv/3	hv/2	hv/4	hv/2
10	Which of the following is true :	$q_{tr}>q_{vib}>q_{ele}>q_{rot}$	$q_{tr}<q_{rot}<q_{vib}<q_{ele}$	$q_{tr}>>q_{rot}>>q_{vib}>>q_{ele}$	$q_{eie}>q_{vib}>q_{rot}>q_{tr}$	$q_{tr}>>q_{rot}>>q_{vib}>>q_{ele}$
11	The canonical partition function of a system of independent indistinguishable particles is given by	$Q =q^N/ N!$	$Q =N! / q^N$	$Q =q^N N!$	$Q =\infty$	$Q =q^N/ N!$
12	The equation for translational partition function is _______________	$q_{tr}= (2\pi m kT / h^2)^{3/2}.V$	$q_{tr}= (2I kT / h^2)$	$q_{tr}= (2\pi m kT / h^2)^{5/2}.V$	$q_{tr}= (2\pi m kT / h^2)^{7/2}.V$	$q_{tr}= (2\pi m kT / h^2)^{3/2}.V$
13	Rotational partition function equation is ___________	$q_{rot}= (2\pi m kT / h^2)^{3/2}.V$	$q_{rot}= 2I kT / h^2$	$q_{rot}= 2 kT / h^2$	$q_{rot}= 2I k / h^2$.	$q_{rot}= 2I kT / h^2$
14	The expression for homonuclear diatomic molecule in Rotational partition function is given by _________	$q_{rot}= 2I kT / \sigma h^2$	$q_{rot}= 2I kT / h^2$	$q_{rot}= 2 kT / h^2$	$q_{rot}= 2I k / h^2$.	$q_{rot}= 2I kT / \sigma h^2$

15	The expression for heteronuclear diatomic molecule in Rotational partition function is given by ________	q_{rot}= 2I kT / σ h^2	q_{rot}= 2 kT / h^2	q_{rot}= 2I kT / h^2	q_{rot}= 2I k / h^2	q_{rot}= 2I kT / h^2
16	The vibrational partition function equation is given by ________	q_{vib} =1/1-$e^{-hυ}$/kT	q_{vib} =1/1+$e^{-hυ}$/kT	q_{vib} =1/1+ $e^{hυ}$/kT	q_{vib} = 1/-1+$e^{-hυ}$/kT	q_{vib} =1/1-$e^{-hυ}$/kT
17	If spins are parallel in rotational partition function to ortho hydrogen then it has __________	even quantum number	odd quantum number	odd and even quantum number	fractional values	even quantum number
18	If spins are antiparallel in rotational partition function to para hydrogen then it has __________	even quantum number	odd quantum number	odd and even quantum number	fractional values	odd quantum number
19	If spins are parallel in ortho hydrogen it has even quantum number then it is said to be ___________	symmetric	antisymmetric	rotational energy	vibrational energy	symmetric
20	If spins are antiparallel in para hydrogen it has odd quantum number then it is said to be ___________	symmetric	antisymmetric	rotational energy	vibrational energy	antisymmetric
21	The translational motion for $Cp,_{tr}$is _________	3/2R	5/2RT	3/2RT	5/2R	5/2R
22	The rotational contribution to $E_{rot}$is _________	RT	R	3/2RT	5/2R	RT

23	The translational motion for $Cv,_{tr}$is _________	3/2R	5/2RT	3/2RT	5/2R	3/2R
24	The rotational contribution for $H_{rot}$is _________	RT	R	5/2R	3/2RT	RT
25	The rotational motion for $Cp,_{rot}$ is _________	RT	R	3/2RT	5/2R	R
26	The translational motion for $H_{tr}$is _________	5/2RT	3/2R	5/2R	R	5/2RT
27	The rotational contribution for $Cv_{rot}$is _________	RT	3/2RT	5/2R	R	R
28	The vibrational contribution to $E_{vib}$is _________	$R.\theta v.1/e^{\theta v}/T-1$	$R (\theta v/T)^{2.}\ e^{\theta v}/T / (e^{\theta v}/T-1)^{2}$	$RT \ln (1-e^{-\theta v}/T)$	$RT \ln (1+ e^{-\theta v}/T)$	$R.\theta v.1/e^{\theta v}/T-1$
29	The vibrational contribution to $C_{vib}$is _________	$R.\theta v.1/e^{\theta v}/T-1$	$R (\theta v/T)^{2.}\ e^{\theta v}/T / (e^{\theta v}/T-1)^{2}$	$RT \ln (1-e^{-\theta v}/T)$	$RT \ln (1+ e^{-\theta v}/T)$	$R (\theta v/T)^{2.}\ e^{\theta v}/T / (e^{\theta v}/T-1)^{2}$
30	The vibrational contribution to $A_{vib}$is _________	$R.\theta v.1/e^{\theta v}/T-1$	$R (\theta v/T)^{2.}\ e^{\theta v}/T / (e^{\theta v}/T-1)^{2}$	$RT \ln (1-e^{-\theta v}/T)$	$RT \ln (1+ e^{-\theta v}/T)$	$RT \ln (1-e^{-\theta v}/T)$
31	5/2R translational equation is _________	$Cp,_{tr}$	H_{tr}	Cv_{tr}	E_{tr}	Cv_{tr}

32	3/2R translational equation is _________	H_{tr}	$Cp,_{tr}$	Cv_{tr}	E_{tr}	Cv_{tr}
33	RT rotational contribution is _________	H_{rot}	$Cv,_{rot}$	G_{rot}	$Cp,_{rot}$	H_{rot}
34	3/2RT translational equation is _________	E_{tr}	Cv_{tr}	G_{tr}	$Cp,_{tr}$	E_{tr}
35	5/2RT translational equation is _________	Cv_{tr}	G_{tr}	H_{tr}	$Cp,_{tr}$	H_{tr}
36	__________ is defined as a collection of a large number of independent assemblies having same temperature , volume and number of identical systems .	canonical ensemble	Grand canonical ensemble	macro canonical ensemble	micro canonical ensemble	canonical ensemble
37	__________ is defined as a collection of a large number of independent assemblies having same temperature , volume and chemical potential.	canonical ensemble	Grand canonical ensemble	macro canonical ensemble	micro canonical ensemble	Grand canonical ensemble
38	If spins are parallel in ______________ to ortho hydrogen then it has even quantum number.	Rotational partition function	vibrational partition function	translational partition function	electronic partition function	Rotational partition function

39	A single particle is referred to as a _______________	system	assembly	ensemble	canonical ensemble	system
40	Collection of particles as a whole is referred to as ________	system	assembly	ensemble	canonical ensemble	assembly
41	The equation $q = \sum g_{i.} e^{-\varepsilon i} /kT$ is ___________	partition function	Stirlings approximation	equipartition law	Maxwell boltzmann distribution law	partition function
42	The equation for __________ partition function is $q_{tr}= (2\pi m kT / h^2)^{3/2}.V$	translational	rotational	vibrational	electronic	translational
43	____________partition function equation is $q_{rot}= 2I kT / h^2$	translational	rotational	vibrational	electronic	rotational
44	The expression for homonuclear diatomic molecule in _____________ partition function is given by $q_{rot}= 2I kT / \sigma h^2$	translational	rotational	vibrational	electronic	rotational
45	The __________motion for $Cp_{,tr\ is}$ 5/2 R.	translational	rotational	vibrational	electronic	translational
46	The ___________contribution to $E_{rot}$is RT	translational	rotational	vibrational	electronic	rotational
47	The _____ motion for $Cv_{,tr}$3/2 R	translational	rotational	vibrational	electronic	translational

48	The __________ contribution for $H_{rot}$is RT.	translational	rotational	vibrational	electronic	rotational
49	The _________ motion for Cp, $_{rot}$ is R.	translational	rotational	vibrational	electronic	rotational
50	The ________ contribution for Cv_{rot} is R.	rotational	translational	vibrational	electronic.	rotational
51	If spins are ----------- in rotational partition function to ortho hydrogen then it has even quantum number	parallel	antiparallel	antisymmetric	non symmetric	parallel
52	The translational motion for -------is 5/2RT	Htr	$Cv,_{tr}$	$Cp,_{tr}$	Gtr	Htr
53	The expression for homonuclear ----------- molecule in rotational partition function is given by q_{rot}= 2I kT / σ h^2	monoatomic	diatomic	triatomic	polyatomic	diatomic
54	3/2RT ------------- equation is $E_{tr.}$	translational	rotational	vibrationa	Electronic	translational
55	If spins are antiparallel in ------------ partition function to para hydrogen then it has odd quantum number	translational	rotational	vibrationa	Electronic	rotational

56	The rotational contribution to ----------is RT	H_{rot}	$E,_{rot}$	$Cp,_{rot}$	G_{rot}	$E,_{rot}$
57	The translational motion for ------------is5/2 R	H_{tr}	$Cv,_{tr}$	$Cp,_{tr}$	G_{tr}	$Cp,_{tr}$
58	The rotational contribution for ------------ is R	H_{rot}	$E,_{rot}$	$Cp,_{rot}$	Cv_{rot}	Cv_{rot}
59	The ------------- ensemble describes an isolated system	Microcanonical	Canonical	Grand Canonical	microstate	Microcanonical
60	The ------------ ensemble describes a system in contact with a heat bath	Microcanonical	Canonical	Grand Canonical	microstate	Canonical

UNIT – IV

SYLLABUS

Partition function: Definition, justification of nomenclature, microcanonical and canonical ensembles. Molecular partition and canonical function. The relation between the total partition function of a molecule and the separate partition functions. Translational partition function, rotational partition function. Effect of molecular symmetry on rotational partition function. Ortho and para hydrogen. Vibrational partition function. Electronic partition function. Evaluation of thermodynamic properties E, H, S, A, G, C_v and C_p from monoatomic and diatomic ideal gas molecules partition functions. Thermodynamic properties of polyatomic ideal gases. Calculation of equilibrium constants of reaction involving ideal gases from partition functions.

Partition function (statistical mechanics)

In statistical mechanics, the **partition function**, Z, is an important quantity that encodes the statistical properties of a system in thermodynamic equilibrium. It is a function of temperature and other parameters, such as the volume enclosing a gas. Most of the aggregate thermodynamic variables of the system, such as the total energy, free energy, entropy, and pressure, can be expressed in terms of the partition function or its derivatives.

There are several different types of partition functions, each corresponding to different types of statistical ensemble. The **canonical partition function** applies to a canonical ensemble, in which the system is allowed to exchange heat with the environment at fixed temperature, volume, and number of particles. The **grand canonical partition function** applies to a grand canonical ensemble, in which the system can exchange both heat and particles with the environment, at fixed temperature, volume, and chemical potential.

Canonical partition function

Definition

Thermodynamically large system is in constant thermal contact with the environment, with a temperature T, and both the volume of the system and the number of constituent particles fixed. This kind of system is called a canonical ensemble. Label with s ($s = 1, 2, 3, \ldots$) the *exact* states (microstates) that the system can occupy, and denote the total energy of the system when it is in microstate s as E_s. Generally, these microstates can be regarded as analogous to discrete quantum states of the system.

The **canonical partition function** is

$$Z = \sum_s e^{-\beta E_s},$$

where the "inverse temperature", β, is conventionally defined as

$$\beta \equiv \frac{1}{k_B T}$$

with k_B denoting Boltzmann's constant. The term $\exp(-\beta \cdot E_s)$ is known as the Boltzmann factor. In systems with multiple quantum states s sharing the same E_s, it is said that the energy levels of the system are degenerate. In the case of degenerate energy levels, partition function in terms of the contribution from energy levels as follows:

$$Z = \sum_j g_j \cdot e^{-\beta E_j},$$

where g_j is the degeneracy factor, or number of quantum states s which have the same energy level defined by $E_j = E_s$.

The above treatment applies to *quantum*statistical mechanics, where a physical system inside a finite-sized box will typically have a discrete set of energyeigenstates, which we can use as the states s above. In *classical* statistical mechanics, it is not really correct to express the partition function as a sum of discrete terms. In classical mechanics, the position and momentum variables of a particle can vary continuously, so the set of microstates is actually uncountable. The partition function described using an integral rather than a sum. For instance, the partition function of a gas of N identical classical particles is

$$Z = \frac{1}{N!} \int \exp[-\beta H(p_1 \cdots p_N, x_1 \cdots x_N)] \, \mathrm{d}^3p_1 \cdots \mathrm{d}^3p_N \, \mathrm{d}^3x_1 \cdots \mathrm{d}^3x_N$$

where

p_i indicate particle momenta
x_i indicate particle positions
d^3 is a shorthand notation serving as a reminder that the p_i and x_i are vectors in three dimensional space, and
H is the classical Hamiltonian.

The partition function is a function of the temperature T and the microstate energies E_1, E_2, E_3, etc. The microstate energies are determined by other thermodynamic variables, such as the number of particles and the volume, as well as microscopic quantities like the mass of the constituent particles. This dependence on microscopic variables is the central point of statistical mechanics. With a model of the microscopic constituents of a system, one can calculate the microstate energies, and thus the partition function, which will then allow us to calculate all the other thermodynamic properties of the system.

The partition function can be related to thermodynamic properties because it has a very important statistical meaning. The probability P_s that the system occupies microstate *s* is

$$P_s = \frac{1}{Z} e^{-\beta E_s}.$$

$e^{-\beta E_s}$ is the well-known Boltzmann factor. The partition function plays the role of a normalizing constant (it does *not* depend on *s*), ensuring that the probabilities sum up to one:

$$\sum_s P_s = \frac{1}{Z} \sum_s e^{-\beta E_s} = \frac{1}{Z} Z = 1.$$

This is the reason for calling *Z* the "partition function": it encodes how the probabilities are partitioned among the different microstates, based on their individual energies. The letter *Z* stands for the "sum over states". This notation also implies the partition function of a system: it counts the (weighted) number of states a system can occupy. Hence if all states are equally probable (equal energies) the partition function is the total number of possible states.

Calculating the thermodynamic total energy

For the partition function, calculate the thermodynamic value of the total energy. This is the expected value, or ensemble average for the energy, which is the sum of the microstate energies weighted by their probabilities:

$$\langle E \rangle = \sum_s E_s P_s = \frac{1}{Z} \sum_s E_s e^{-\beta E_s} = -\frac{1}{Z} \frac{\partial}{\partial \beta} Z(\beta, E_1, E_2, \cdots) = -\frac{\partial \ln Z}{\partial \beta}$$

or, equivalently,

$$\langle E \rangle = k_B T^2 \frac{\partial \ln Z}{\partial T}.$$

Incidentally, if the microstate energies depend on a parameter λ in the manner

$$E_s = E_s^{(0)} + \lambda A_s \qquad \text{for all } s$$

then the expected value of *A* is

$$\langle A\rangle = \sum_s A_s P_s = -\frac{1}{\beta}\frac{\partial}{\partial\lambda}\ln Z(\beta,\lambda).$$

This provides us with a method for calculating the expected values of many microscopic quantities. Add the quantity to the microstate energies (quantum mechanics, to the Hamiltonian), calculate the new partition function and expected value, and then set λ to zero in the final expression..

Relation to thermodynamic variables

The relationships between the partition function and the various thermodynamic parameters of the system.

The thermodynamic energy is

$$\langle E\rangle = -\frac{\partial \ln Z}{\partial\beta}.$$

The variance in the energy (or "energy fluctuation") is

$$\langle(\Delta E)^2\rangle \equiv \langle(E-\langle E\rangle)^2\rangle = \frac{\partial^2 \ln Z}{\partial\beta^2}.$$

The heat capacity is

$$C_v = \frac{\partial\langle E\rangle}{\partial T} = \frac{1}{k_B T^2}\langle(\Delta E)^2\rangle.$$

The entropy is

$$S \equiv -k_B\sum_s P_s \ln P_s = k_B(\ln Z + \beta\langle E\rangle) = \frac{\partial}{\partial T}(k_B T\ln Z) = -\frac{\partial A}{\partial T}$$

where$A$ is the Helmholtz free energy defined as $A = U - TS$, where $U=<E>$ is the total energy and S is the entropy, so that

$$A = \langle E\rangle - TS = -k_B T\ln Z.$$

Partition functions of subsystems

Suppose a system is subdivided into N sub-systems with negligible interaction energy. If the partition functions of the sub-systems are ζ_1, ζ_2, ...,ζ_N, then the partition function of the entire system is the *product* of the individual partition functions:

$$Z = \prod_{j=1}^{N} \zeta_j.$$

If the sub-systems have the same physical properties, then their partition functions are equal, $\zeta_1 = \zeta_2 = ... = \zeta$, in which case

$$Z = \zeta^N.$$

If the sub-systems are actually identical particles, in the quantum mechanical sense that they are impossible to distinguish even in principle, the total partition function must be divided by a N ! (Nfactorial):

$$Z = \frac{\zeta^N}{N!}.$$

Grand canonical partition function

Definition

Definition of the canonical partition function for the canonical ensemble, defining a **grand canonical partition function** for a grand canonical ensemble, a system that can exchange both heat and particles with the environment, which has a constant temperature T, and a chemical potential μ. The grand canonical partition function, although conceptually more involved, simplifies the theoretical handling of quantum systems because it incorporates in a simple way the spin-statistics of the particles (i.e. whether particles are bosons or fermions

The grand canonical partition function $\mathcal{Z}$for an ideal quantum gas (a gas of non-interacting particles in a given potential well) is given by the following expression:

$$\mathcal{Z} = \sum_{N=0}^{\infty} \sum_{\{n_i\}} \prod_i \; e^{-\beta n_i(\epsilon_i - \mu)}$$

where N is the total number of particles in the gas, index i runs over every microstate (that is, a single particle state in the potential) with n_i being the number of particles occupying microstate i and ε_i being the energy of a particle in that microstate. The set $\{ n_i \}$ is the collection of all possible occupation numbers for each of these microstates such that $\Sigma\, n_i = N$.

For example, consider the $N = 3$ term in the above sum. One possible set of occupation numbers would be $n_i = 0, 1, 0, 2, 0 ...$ and the contribution of this set of occupation numbers to the $N = 3$ term would be

$$\prod_i e^{-\beta n_i(\epsilon_i-\mu)} = e^{-\beta(\epsilon_1-\mu)}\, e^{-2\beta(\epsilon_3-\mu)}.$$

For bosons, the occupation numbers can take any integer values as long as their sum is equal to N. For fermions, the Pauli exclusion principle requires that the occupation numbers only be 0 or 1, again adding up to N.

Probability

The expression for the grand partition function

$$\mathcal{Z} = \prod_i \mathcal{Z}_i.$$

(The product is sometimes taken over all states with equal energy, rather than over each state, in which case the individual partition functions must be raised to a power g_i where g_i is the number of such states. g_i is also referred to as the "degeneracy" of states.)

For a system composed of bosons:

$$\mathcal{Z}_i = \sum_{n_i=0}^{\infty} e^{-\beta n_i(\epsilon_i-\mu)} = \frac{1}{1-e^{-\beta(\epsilon_i-\mu)}}$$

and for a system composed of fermions:

$$\mathcal{Z}_i = \sum_{n_i=0}^{1} e^{-\beta n_i(\epsilon_i-\mu)} = 1 + e^{-\beta(\epsilon_i-\mu)}.$$

Maxwell-Boltzmann gas, we must use "correct Boltzmann counting" and divide the Boltzmann factor $e^{-\beta(\epsilon_i-\mu)}$ by $n_i!$.

$$\mathcal{Z}_i = \sum_{n_i=0}^{\infty} \frac{e^{-\beta n_i(\epsilon_i-\mu)}}{n_i!} = \exp\left(e^{-\beta(\epsilon_i-\mu)}\right).$$

Relation to thermodynamic variables

With the canonical partition function, the grand canonical partition function can be used to calculate thermodynamic and statistical variables of the system. As with the canonical ensemble, the thermodynamic quantities are not fixed, but have a statistical distribution about a mean or expected value.

The most probable occupation numbers are:

$$\langle n_i \rangle = -\left(\frac{\partial \ln(\mathcal{Z}_i)}{\partial \alpha}\right)_{\beta,V} = \frac{1}{\beta}\left(\frac{\partial \ln(\mathcal{Z}_i)}{\partial \mu}\right)_{\beta,V},$$

where $\alpha = -\beta \cdot \mu$.

For Boltzmann particles this yields:

$$\langle n_i \rangle = e^{-\beta(\epsilon_i - \mu)}.$$

For bosons:

$$\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1}.$$

For fermions:

$$\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1}.$$

which are just the results found using the canonical ensemble for Maxwell-Boltzmann statistics, Bose-Einstein statistics and Fermi-Dirac statistics, respectively.

Total number of particles

$$\langle N \rangle = -\left(\frac{\partial \ln(\mathcal{Z})}{\partial \alpha}\right)_{\beta,V} = \frac{1}{\beta}\left(\frac{\partial \ln(\mathcal{Z})}{\partial \mu}\right)_{\beta,V}.$$

Variance in total number of particles

$$\langle (\delta N)^2 \rangle = \left(\frac{\partial^2 \ln(\mathcal{Z})}{\partial \alpha^2}\right)_{\beta,V}.$$

Internal energy

$$\langle E \rangle = -\left(\frac{\partial \ln(\mathcal{Z})}{\partial \beta}\right)_{\mu,V} + \mu \langle N \rangle.$$

Variance in internal energy

$$\langle (\delta E)^2 \rangle = \left(\frac{\partial^2 \ln(\mathcal{Z})}{\partial \beta^2} \right)_{\mu, V}.$$

Pressure

$$PV = k_B T \ln \mathcal{Z}.$$

Mechanical equation of state

$$\langle PV \rangle = \frac{\ln(\mathcal{Z})}{\beta}.$$

Relation to potential V

For the case of a non-interacting gas, using the "Semiclassical Approach" we can write (approximately) the inverse of the potential in the form:

$$\frac{1}{2i\pi} \int_{c-i\infty}^{c+i\infty} \mathrm{d}s \frac{Z(s)}{\sqrt{(\pi s)}} e^{st} \sim V^{-1}(t)$$

$s = \dfrac{1}{k_B T}$ (valid for high T)

The Hamiltonian of every particle is H=T+V .

Sackur–Tetrode equation

The Sackur–Tetrode equation is an expression for the entropy of a monatomic classical ideal gas which incorporates quantum considerations .The Sackur–Tetrode equation is named for Hugo Martin Tetrode (1895–1931) and Otto Sackur (1880–1914), who developed it independently as a solution of Boltzmann's gas statistics and entropy equations.

The Sackur–Tetrode equation is written:

$$S = kN \ln \left[\left(\frac{V}{N} \right) \left(\frac{U}{N} \right)^{\frac{3}{2}} \right] + \frac{3}{2} kN \left(\frac{5}{3} + \ln \frac{4\pi m}{3h^2} \right)$$

where$V$ is the volume of the gas, N is the number of particles in the gas, U is the internal energy of the gas, k is Boltzmann's constant, m is the mass of a gas particle, h is Planck's constant.

The Sackur–Tetrode equation can also be expressed in terms of the thermal wavelength Λ. Using the classical ideal gas relationship $U = (3/2)NkT$ for a monatomic gas gives

$$\frac{S}{kN} = \ln \left[\frac{V}{N\Lambda^3} \right] + \frac{5}{2}$$

The assumption was made that the gas is in the classical regime, and is described by Maxwell–Boltzmann statistics.From the thermal wavelength, the Sackur–Tetrode equation is only valid for

$$\frac{V}{N\Lambda^3} \gg 1.$$

the entropy predicted by the Sackur–Tetrode equation approaches negative infinity as the temperature approaches zero.

Sackur–Tetrode constant

The **Sackur–Tetrode constant**, written S_0/R, is equal to S/kN evaluated at a temperature of $T = 1$ kelvin, at standard pressure (100 kPa or 101.325 kPa, to be specified), for one mole of an ideal gas composed of particles of mass equal to one atomic mass unit.

Useful Information and Some Simple Models

$$q = q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vib}} \cdot q_{\text{elec}} \cdot q_{\text{etc.}},$$

whereq_{etc} is the partition function.

For a gas of N molecules,

$$Q = \frac{q^N}{N!} = \frac{q_{\text{trans}}^N}{N!} \cdot q_{\text{rot}}^N \cdot q_{\text{vib}}^N \cdot q_{\text{elec}}^N \cdot q_{\text{etc.}}^N.$$

q's in the last two equations are **multiplied** together and not added.

The thermodynamic functions as a sum of contributions from the different types of motion, translation, rotation, and etc. That is

$$A = A_{\text{trans}} + A_{\text{rot}} + A_{\text{vib}} + A_{\text{elec}} + \cdots.$$

For example the rotational contribution to internal energy or entropy or any other function can be obtained from

$$\begin{aligned} A_{\text{rot}} &= -kT \ln q_{\text{rot}}^N \\ &= -NkT \ln q_{\text{rot}}, \end{aligned}$$

There is no $N!$ inthis equation.

$N!$, to use Stirling's approximation, which can be written

$$\ln N! \approx N \ln N - N,$$

Or

$$N! \approx N^N e^{-N}.$$

This approximation is useful when N is **very** large, like around Avogadro's number.

Using Stirling's approximation makes the translational part of the partition function,

$$Q_{\text{trans}} = \left(\frac{q_{\text{trans}} e}{N} \right)^N,$$

Translational Motion In One Dimension

The translational part of the motion of a molecule by particle-in-a-box states. The energy of a particle in a one-dimensional of length, l, box depends on one quantum number, n, which can be 1, 2, 3, . . . up to infinity. The equation for the quantized energy is,

$$E_n = \frac{h^2 n^2}{8ml^2},$$

where*h* is Planck's constant and *m* is the mass of one molecule.

The partition function for this system is,

$$q = \sum_n e^{-\beta \frac{h^2 n^2}{8ml^2}}.$$

The summation cannot be performed in closed form but it can be approximated by an integral to high accuracy,

$$q = \int_0^\infty e^{-\beta \frac{h^2 n^2}{8ml^2}} dn.$$

This integral can be evaluated and gives

$$q \approx \left(\frac{2\pi mkt}{h^2} \right)^{\frac{1}{2}} l.$$

Translational Motion In Three Dimensions

Translational motion in three dimensions there are three quantum numbers, one for each direction, n_x, n_y, and n_z, and the energy is

$$E_{n_x n_y n_z} = \frac{h^2}{8ml^2} \left(n_x^2 + n_y^2 + n_z^2 \right)$$

The translational partition function in three dimensions is a three–fold summation

$$q_{\text{trans}} = \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{-\beta \frac{h^2}{8ml^2}\left(n_x^2 + n_y^2 + n_z^2\right)}.$$

This equationcan be written as

$$q_{\text{trans}} = \left(\sum_n e^{-\beta \frac{h^2 n^2}{8ml^2}} \right)^3 .$$

Since already approximated the summation in Equation by an integral immediately write

$$q_{\text{trans}} \approx \left(\frac{2\pi mkt}{h^2} \right)^{\frac{3}{2}} V$$

where let $l^3 = V$

The rotational energy of a linear molecule (neglecting such things as centrifugal distortion) is given by $BJ(J+1)$ and each J level is $2J+1$ degenerate. The rotational partition function is easy to write,

$$q_{\text{rot}} = \sum_J (2J+1) e^{-\beta BJ(J+1)} .$$

If $\beta B << 1$ (this is the high temperature limit) the summation can be approximated by an integral to give

$$q_{\text{rot}} \approx \frac{1}{\beta B} = \frac{kT}{B} .$$

For a heteronuclear diatomic molecule (or an unsymmetrical one, like HCN) have to rotate the molecule all the way around 360° to bring it back to the same "state." For a homonuclear diatomic molecule (or a symmetrical one, such as CO_2) it comes back to the same "state" after only 180° rotation. So an asymmetric molecule, in going around 360° has only passed through one "state," while a symmetric molecule has passed through two "states" in a 360° rotation.

$$q_{\text{rot}} \approx \frac{kT}{B\sigma} ,$$

whereσ is called the symmetry number. σ is the number of ways the molecule can be oriented which are indistinguishable from each other. For HCl, $\sigma = 1$; and for Cl_2, $\sigma = 2$ (as long as both Cl atoms are the same isotope).

The "characteristic rotational temperature," Θ_R, as

$$\Theta_{\mathrm{R}} = \frac{B}{k},$$

so that the rotational partition function can be written,

$$q_{\mathrm{rot}} \approx \frac{T}{\sigma \Theta_{\mathrm{R}}}.$$

Θ_R also allows high and low temperatures. If $T >> \Theta_R$ say that T is a high temperature .If $T \approx \Theta_R$ or $T < \Theta_R$, then say T is a low temperature and we must use the summation formula (divided by the appropriate σ). For reasonable size molecules Θ_R is usually only a few degrees Kelvin. For light molecules it can be higher (for H_2, $\Theta_R = 87.57$ K).

Nonlinear molecules have three moments of inertia and three rotational constants (and, hence, three Θ_R's). The three rotational constants A, B, and C, the rotational partition function (at high temperatures) is

$$q_{\mathrm{rot}} \approx \frac{\sqrt{\pi}}{\sigma} \frac{(kT)^{\frac{3}{2}}}{\sqrt{ABC}}.$$

σ is the symmetry number and it is the number of orientations of the molecule which are indistinguishable from each other (for benzene σ =12, for ammonia σ =3, etc).

Vibrational motion

Vibrational energies for one mode of vibration are

$$E_{\mathrm{v}} = h\nu(\mathrm{v} + \frac{1}{2}),$$

where v = 0, 1, 2, 3, . . . , and $\nu$is the characteristic frequency of the oscillator. The vibrational partition function is

$$q_{\text{vib}} = \sum_{\text{v}} e^{-\beta h\nu(\text{v}+1/2)}$$

$$= e^{-\beta h\nu/2} \sum_{\text{v}} e^{-\beta h\nu \text{v}},$$

which can be summed in closed form to give

$$q_{\text{vib}} = e^{-\beta h\nu/2} \frac{1}{1-e^{-\beta h\nu}}.$$

$$e^{-\beta h\nu\text{v}} = \left(e^{-\beta h\nu}\right)^{\text{v}}.)$$

Sometimes a characteristic vibrational temperature, Θ_v, is defined by

$$\Theta_{\text{v}} = \frac{h\nu}{k},$$

and the partition function is written in terms of Θ_v instead of $h\nu/k$. Characteristic vibrational temperatures are usually several thousands of Kelvins except for very "soft" or low frequency vibrational modes.

Polyatomic molecules have more than one vibrational mode. For polyatomic molecules each mode (all multiplied together, not added!).

The high temperature limit of q_{vib} (ignoring the zero−point energy contribution) is T/Θ_v. This is sometimes called the "classical" limit because it is the result that is obtained from statistical thermodynamics from classical mechanics instead of quantum mechanics.

Electronic Energy

Electronic excited state energies are usually (but not always) much higher than kT, so they don't contribute to thermodynamic properties except at extremely high temperatures. When they contribute have to write out the partition function term−by−term

$$q_{\text{elec}} = g_1 + g_2 e^{-\beta E_2} + g_3 e^{-\beta E_3} + \cdots.$$

Here g_i is the degeneracy of the i'th level, and selected the ground electronic state as the zero (or origin) of energy.

$$Q = \sum_j e^{-\beta E_j}.$$

If shift each level by the same constant amount, the levels E_j + c, looks like a new partition function

$$Q' = \sum_j e^{-\beta(E_j + c)}.$$

But this factors to give

$$Q' = e^{-\beta c} \sum_j e^{-\beta E_j}.$$

When we take lnQ' see that it differs from ln$Q$ only by an additive term $-\beta c$. This term will contribute a constant additive term to A, U, H, and G, but it will not contribute to the entropy or the heat capacities, nor will it contribute to quantities like ΔA, etc.

$$A - A_0 = -kT \ln Q,$$

and they continue in the same manner with U, G, and etc. There is always an arbitrary zero of energy

$$A = -kT \ln Q,$$

Equilibrium Constants

The equilibrium constants (in terms of concentration in molecules/m^3) from partition functions. The expression for this concentration equilibrium constant, in terms of the material, for a hypothetical reaction,

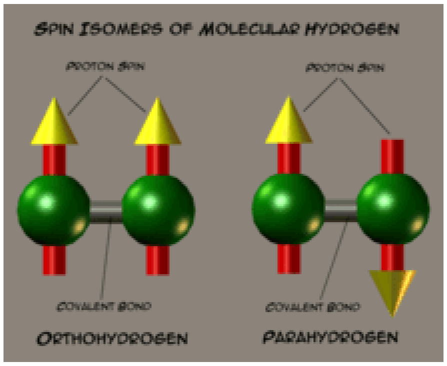
$$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D},$$

is,

$$K = \frac{\left(\frac{q_\mathrm{C}}{V}\right)^c \left(\frac{q_\mathrm{D}}{V}\right)^d}{\left(\frac{q_\mathrm{A}}{V}\right)^a \left(\frac{q_\mathrm{B}}{V}\right)^b}.$$

The volume dividing each of the molecular partition functions cancel the volume occurring in the translational part of the partition function, so that there is no explicit volume dependence in K. This equilibrium constant will be in units of molecules/m^3 to some power (the $-c - d + a + b$ power, actually). It can be converted to mol/L or pressure by standard methods. Recall that $N/V = p/kT$.

Spin isomers of hydrogen



Spin Isomers of Molecular Hydrogen

Molecular hydrogen occurs in two isomeric forms, one with its two proton spins aligned parallel (orthohydrogen), the other with its two proton spins aligned antiparallel (parahydrogen). At room temperature and thermal equilibrium, hydrogen consists of 25% parahydrogen and 75% orthohydrogen.

Nuclear spin states of H_2

Each hydrogenmolecule (H_2) consists of two hydrogen atoms linked by a covalent bond. If we neglect the small proportion of deuterium and tritium which may be present, each hydrogen atom consists of one proton and one electron. The proton has an associated magnetic moment, which is associated with the proton's spin. In the H_2 molecule, the spins of the two hydrogen nuclei (protons) couple to form a triplet state ($I = 1$, $\alpha_1\alpha_2$, $(\alpha_1\beta_2 + \beta_1\alpha_2)/(2^{1/2})$, or $\beta_1\beta_2$ for which $M_I = 1, 0, -1$ respectively — this is **orthohydrogen**) or to form a singlet state ($I = 0$, $(\alpha_1\beta_2 - \beta_1\alpha_2)/(2^{1/2})$ $M_I = 0$ — this is **parahydrogen**). The ratio between the ortho and para forms is about 3:1 at standard temperature and pressure - a reflection of the spin degeneracy ratio, but if thermal equilibrium between the two forms is established, the para form dominates at low temperatures (approx. 99.8% at 20 K. Other molecules and functional groups containing two hydrogen atoms, such as water and methylene, also have ortho and para forms (e.g. orthowater and parawater), although their ratios differ from that of the dihydrogen molecule.

Thermal properties

The permutationalantisymmetry of the H_2wavefunction (protons are fermions) imposes restrictions on the possible rotational states the two forms of H_2 can adopt. Orthohydrogen, with symmetric nuclear spin func

tions, can only have rotational wavefunctions that are antisymmetric with respect to permutation of the two protons. Conversely, parahydrogen with an antisymmetric nuclear spin function, can only have rotational wavefunctions that are symmetric with respect to permutation of the two protons. Applying the rigid rotor approximation, the energies and degeneracies of the rotational states are given by

$$E_J = \frac{J(J+1)\hbar^2}{2I}; \; g_J = 2J+1 .$$

The rotational partition function is conventionally written as

$$Z_{\text{rot}} = \sum_{J=0}^{\infty} g_J e^{-E_J/k_B T} .$$

However, as long as these two spin isomers are not in equilibrium, it is more useful to write separate partition functions for each,

$$Z_{\text{para}} = \sum_{\text{even } J} (2J+1)e^{-J(J+1)\hbar^2/2Ik_BT} \; ; Z_{\text{ortho}} = 3\sum_{\text{odd } J} (2J+1)e^{-J(J+1)\hbar^2/2Ik_BT}$$

.

The factor of 3 in the partition function for orthohydrogen accounts for the spin degeneracy associated with the +1 spin state. When equilibrium between the spin isomers is possible, then a general partition function incorporating this degeneracy difference can be written as

$$Z_{\text{equil}} = \sum_{J=0}^{\infty} (2-(-1)^J)(2J+1)e^{-J(J+1)\hbar^2/2Ik_BT}$$

The molar rotational energies and heat capacities are derived for any of these cases from

$$U_{\text{rot}} = RT^2 \left(\frac{\partial \ln Z_{\text{rot}}}{\partial T}\right) \; ; C_{v,\,\text{rot}} = \left(\frac{\partial U_{\text{rot}}}{\partial T}\right)$$

The antisymmetry-imposed restriction on possible rotational states, orthohydrogen has residual rotational energy at low temperature wherein nearly all the molecules are in the J = 1 state (molecules in the symmetric spin-triplet state cannot fall into the lowest, symmetric rotational state) and possesses nuclear-spin entropy due to the triplet state's threefold degeneracy. The residual energy is significant because the rotational energy levels are relatively widely spaced in H_2; the gap between the first two levels when expressed in temperature units is twice the rotational temperature for H_2,

$$\frac{E_{J=1}-E_{J=0}}{k_B}=2\theta_{rot}=\frac{\hbar^2}{k_B I}=174.98\ \mathrm{K}.$$

This is the T = 0 intercept seen in the molar energy of orthohydrogen. This residual energy, 1091 J/mol, is somewhat larger than the enthalpy of vaporization of normal hydrogen, 904 J/mol at the boiling point, T_b = 20.369 K (this refers to the "normal", room-temperature, 3:1 ortho:para mixture. The boiling points of parahydrogen and normal (3:1) hydrogen are nearly equal; for parahydrogen ΔH_{vap} = 898 J/mol at T_b = 20.277 K. It follows that nearly all the residual rotational energy of orthohydrogen is retained in the liquid state. Orthohydrogen is consequently unstable at low temperatures and spontaneously converts into parahydrogen, but the process is slow in the absence of a magnetic catalyst to facilitate interconversion of the singlet and triplet spin states. At room temperature, hydrogen contains 75% orthohydrogen, a proportion which the liquefaction process preserves if carried out in the absence of a catalyst like ferric oxide, activated carbon, platinized asbestos, rare earth metals, uranium compounds, chromic oxide, or some nickel compounds to accelerate the conversion of the liquid hydrogen into parahydrogen, or supply additional refrigeration equipment to absorb the heat that the orthohydrogen fraction will release as it spontaneously converts into parahydrogen.

Thermodynamic properties of Polyatomic Gas

The evaluation of thermodynamic properties for a gaseous assembly composed of polyatomicmolecules depends on whether the associated molecular structure is linear or nonlinear.For linear molecules, the relevant atoms are arranged along a single Cartesian coordinate; examples are CO_2, N_2O, and C_2H_2. Purely geometrical considerations restrict linearpolyatomics to two rotational degrees of freedom (as for diatomics), while nonlinearpolyatomics exhibit three such degrees of freedom. Hence, for a polyatomic moleculecomposed of $n$individual atoms, the number of vibrational modes must be $3n-5$ for thelinear case and $3n-6$ for the nonlinear case.

Degrees of freedom for a polyatomic molecule with n atoms

Mode	Linear	Nonlinear
Translation	3	3
Rotation	2	3
Vibration	$3n-5$	$3n-6$

Each vibrational mode of a polyatomic molecule designates an internuclear distance or angle whose oscillation reflects a local electronic potential. Hence, stable molecular configurations for complex molecules must correspond to minima on a multidimensional potential surface.This perspective, however, is much too difficult to handle from a quantum mechanical viewpoint; therefore, as for the diatomic case, we seek a simpler model reflecting available spectroscopic data. The rigid-rotor/harmonic oscillator model, thus fostering complete separation of energy modes. A fully complex model, including any rovibrational coupling, must obviously be employed for more rigorous calculations. Assuming complete mode separation, the molecular partition function for a polyatomic molecule

$$Z = Z_{tr} Z_{el} Z_{rot} Z_{vib}.$$

The translational contribution, similar to that for a diatomic molecule, is given by

$$Z_{tr} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V \qquad m = \sum_i m_i.$$

where the total mass, *m*, is simply the sum of all atomic masses composing the molecule. Therefore, we conclude that the contribution of the translational mode to thermodynamic properties is essentially the same for a polyatomic molecule as for the monatomic gas. For nearly all polyatomics, the energy ascribed to the first excited electronic level is sufficiently high that only the ground electronic state is necessary for most property calculations. The electronic partition function becomes

$$Z_{el} = \sum_j g_j e^{-\varepsilon_j/kT} \simeq g_0$$

The resulting contribution to thermodynamic properties isnonzero only for the entropy and free energies. The required electronic degeneracy canbe obtained, as usual, from the term symbol associated with the ground electronic state.

For linear polyatomics, the term symbol and degeneracy follow the diatomic molecules. However, for nonlinear polyatomics, the degeneracy is always

$$g_{el} = 2S + 1$$

as obtained from the associated term symbol

$$^{2S+1}A_i \text{ or } ^{2S+1}B_i \qquad i = 1,\ 2$$

.

Here, *A* indicates a symmetric while *B* implies a non-symmetric molecular wave function. Similarly, the index *i* = 1, 2 designates whether this wave function is symmetric or asymmetric, respectively, with respect to the chemical structure of the polyatomic molecule.

	Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answers
1	According to Debye theory,in the limit T→0 Cv of a monoatomic crystal is proportional to__________	T	T^2	T^3	T^4	T^3
2	According to Dulong-petits law, for a monoatomic crystal, Cv/cal K^{-1} mol^{-1} is ________	5	4	6	5	6
3	Which of the following are fermions :	electron	^2D	$^4He_2$	a gas at high temperature.	electron
4	Which of the following are bosons :	proton	$^4He_2$	$^{19}D_9$	electrons	$^4He_2$
5	Which is a boltzon (maxwellon)	electron	proton	^2D	a gas at high temperature	a gas at high temperature
6	Which of the following are fermions :	^2D	proton	$^4He_2$	a gas at high temperature	proton
7	Which of the following are bosons :	proton	^2D	$^{19}F_9$	electrons	^2D
8	If g_i and n_i are respectively, the degeneracy and occupation number of the ith energy level,	$g_i/ n_{i<<1}$	$g_i/ n_{i>>1}$	g_i/ n_iisindeterminate	$g_i/ n_{i<0}$	$g_i/ n_{i>>1}$

	then the conditions under which M-B, F-D, and B.E statistics give identical results is ______					
9	The partition function for 1 D.H.O. equation is ___________	$1/1-e^{-h\upsilon}/kT$	$(1/1-e^{-h\upsilon}/kT)^3$	$1/1-e^{h\upsilon}/kT$	$(1/1-e^{h\upsilon}/kT)^3$	$1/1-e^{-h\upsilon}/kT$
10	The partition function for 3 D.H.O. equation is ___________	$1/1-e^{-h\upsilon}/kT$	$(1/1-e^{-h\upsilon}/kT)^3$	$1/1-e^{h\upsilon}/kT$	$(1/1-e^{h\upsilon}/kT)^3$	$(1/1-e^{-h\upsilon}/kT)^3$
11	The Bose Einstein statistics equation is ____________	$N_i= g_i / e^{\alpha} .e^{\beta\varepsilon\acute{\iota}}-1$	$N_i= g_i / e^{\alpha} .e^{\beta\varepsilon\acute{\iota}}+1$	$N_i= g_i / e^{\beta\varepsilon\acute{\iota}}-1$	$N_i= g_i / e^{-\alpha} e^{-\beta\varepsilon\acute{\iota}}$	$N_i= g_i / e^{\alpha} .e^{\beta\varepsilon\acute{\iota}}-1$
12	The Fermi Dirac statistics equation is ____________	$N_i= g_i / e^{\alpha} .e^{\beta\varepsilon\acute{\iota}}-1$	$N_i= g_i / e^{\alpha} .e^{\beta\varepsilon\acute{\iota}}+1$	$N_i= g_i / e^{\beta\varepsilon\acute{\iota}}-1$	$N_i= g_i / e^{-\alpha} e^{-\beta\varepsilon\acute{\iota}}$	$N_i= g_i / e^{\alpha} .e^{\beta\varepsilon\acute{\iota}}+1$
13	F.D. statistics wave functions is _______	Symmetric	antisymmetric	both	none	antisymmetric
14	B.E. statistics wave functions is _______	Symmetric	antisymmetric	both	none	Symmetric
15	F.D. statistics having spins _______	1/2 ,3/2 ,5/2	0, 1,2,3	2,4,6	4/2 ,6/2 .	1/2 ,3/2 ,5/2
16	B.E. statistics having spins _______	1/2 ,3/2 ,5/2	0, 1,2,3	2,4,6	4/2 ,6/2 .	0, 1,2,3

17	In F.D. statistics only _____ particle can occupy each quantum state.	one	two	five	three	one
18	Einstein assumed that all the particles in a crystal vibrate with ________ frequency.	different	same	high	low	same
19	Einstein equation gives results that are too _______ at low temperature.	low	high	very high	very low.	low
20	Debye's characteristic temperature is given as θ_D =	$h\nu_m/k$	$- h\nu_m/k$	$2h\nu_m/k$	$5\ h\nu_m/k$	$h\nu_m/k$
21	Debye's T-cubed law equation is Cv = _______	$463.5\ (T/\ \theta_D)^3$ cal /deg	$423.5\ (T/\ \theta_D)^3$ cal /deg	$224.5\ (T/\ \theta_D)^3$ cal /deg	$425.5\ (T/\ \theta_D)^3$ cal /deg	$463.5\ (T/\ \theta_D)^3$ cal /deg
22	Planck distribution law for the black body radiation equation is _____	$\rho(\nu)d\nu = 8\pi h\nu/c^3.\ \nu^2/\ e^{h\upsilon}/kT-1\ .d\ \nu$	$\rho(\nu)d\nu = 8\pi h\nu/c^3.\ \nu^2/\ e^{-h\upsilon}/kT-1\ .d\ \nu$	$\rho(\nu)d\nu = 8\pi h\nu/c^3.\ \nu^2/\ e^{-h\upsilon}/kT+1\ .d\ \nu$	$\rho(\nu)d\nu = 8\pi h\nu/c^3.\ \nu^2/\ -e^{-h\upsilon}/kT-1\ .d\ \nu$	$\rho(\nu)d\nu = 8\pi h\nu/c^3.\ \nu^2/\ e^{h\upsilon}/kT-1\ .d\ \nu$
23	The heat capacity of electrons in metal equation is ___________	$C_{v,ele} = 2R.k.T/\ \epsilon_F$	$C_{v,ele} = 2.k.T/\ \epsilon_F$	$C_{v,ele} = -2.k.T/\ \epsilon_F$	$C_{v,ele} = 2.k.\ /\ \epsilon_F$	$C_{v,ele} = 2R.k.T/\ \epsilon_F$
24	Maxwell Boltzmann statistics equation is _______	$N_i= g_i\ /\ e^{\alpha}\ .e^{\beta\varepsilon\acute{\iota}}-1$	$N_i= g_i\ /\ e^{\alpha}\ .e^{\beta\varepsilon\acute{\iota}}$	$N_i= g_i\ /\ e^{\alpha}\ e^{\beta\varepsilon\acute{\iota}}+1$	$N_i= g_i\ /\ e^{-\alpha}\ e^{-\beta\varepsilon\acute{\iota}}+1$	$N_i= g_i\ /\ e^{\alpha}\ .e^{\beta\varepsilon\acute{\iota}}$
25	Dulongpetits law only a limiting law applicable at __________ temperature.	high	low	very high	very low.	high

26	System possessing wave functions are photons,atoms or molecules with even number of nucleons in their nuclei is ___________	Maxwell Boltzmann statistics	Fermi Dirac statistics	Bose Einstein statistics	Debye equation	Bose Einstein statistics
27	System possessing wave functions are electrons, protons, atoms or molecules with odd number of nucleons in their nuclei is ___________	Maxwell Boltzmann statistics	Fermi Dirac statistics	Bose Einstein statistics	Debye equation.	Fermi Dirac statistics
28	Entropy of B.E. gas equation is S = _______	$Nk\alpha + k\beta E + Nk$	$Nk\alpha - k\beta E + Nk$	$Nk\alpha + k\beta E - Nk$	$-Nk\alpha - k\beta E + Nk$	$Nk\alpha + k\beta E + Nk$
29	.B.E. statistics equation is _____________	$g_i / N_i + 1 = e^{\alpha} . e^{\beta\varepsilon i}$	$g_i / N_i - 1 = e^{\alpha} . e^{\beta\varepsilon i}$	$g_i / N_i = e^{\alpha} . e^{\beta\varepsilon i}$	$g_i / N_i = e^{-\alpha} . e^{-\beta\varepsilon i}$	$g_i / N_i + 1 = e^{\alpha} . e^{\beta\varepsilon i}$
30	F.D. statistics equation is _____________	$g_i / N_i = e^{\alpha} . e^{\beta\varepsilon i}$	$g_i / N_i - 1 = e^{\alpha} . e^{\beta\varepsilon i}$	$g_i / N_i + 1 = e^{\alpha} . e^{\beta\varepsilon i}$	$g_i / N_i = e^{-\alpha} . e^{-\beta\varepsilon i}$	$g_i / N_i - 1 = e^{\alpha} . e^{\beta\varepsilon i}$
31	M.B. statistics equation is _____________	$g_i / N_i - 1 = e^{\alpha} . e^{\beta\varepsilon i}$	$g_i / N_i + 1 = e^{\alpha} . e^{\beta\varepsilon i}$	$g_i / N_i = e^{\alpha} . e^{\beta\varepsilon i}$	$g_i / N_i = e^{-\alpha} . e^{-\beta\varepsilon i}$	$g_i / N_i = e^{\alpha} . e^{\beta\varepsilon i}$
32	Systems having spins of ½,3/2,5/2 are called ___________	Bosons	Fermions	Maxwellons	B.E. statistics	Fermions
33	Systems having spins of 0,1,2,3 are called ___________	Bosons	Fermions	Maxwellons	F.D. statistics	Bosons
34	Electron is an example for _______________	Bosons	Fermions	Maxwellons	B.E. statistics	Fermions

35	$^4He_2$ is an example for ________________	Fermions	Maxwellons	Bosons	F.D. statistics	Bosons
36	A gas at high temperature is an example for __________	Fermions	Maxwellons	Bosons	F.D. statistics	Maxwellons
37	Proton is an example for _________	Fermions	Maxwellons	Bosons	B.E. statistics	Fermions
38	^2D is an example for _________	Bosons	Fermions	Maxwellons	F.D. statistics	Bosons
39	$N_i = g_i / e^{\alpha} . e^{\beta\varepsilon i} - 1$ equation is called _________	B.E. statistics	F.D. statistics	M.B. statistics	Maxwellons	B.E. statistics
40	$N_i = g_i / e^{\alpha} . e^{\beta\varepsilon i} + 1$ equation is called _________	B.E. statistics	F.D. statistics	M.B. statistics	Maxwellons.	F.D. statistics
41	According to Debye theory,in the limit T→0 _________ of a monoatomic crystal is proportional to T^3.	Cv	Cp	S	E	Cv
42	The equation $1/1-e^{-h\upsilon}/kT$ is the partition function for ____________	1 D.H.O.	3 D.H.O.	2 D.H.O	translational function	1 D.H.O.
43	In _________ statistics only one particle can occupy each quantum state.	Fermi Dirac	Bose Einstein	Debye's	Bohr	Fermi Dirac

44	_____________assumed that all the particles in a crystal vibrate with same frequency	Debye’s	Fermi Dirac	Einstein	Bohr	Einstein
45	The equation $Cv = 463.5 (T/ \theta_D)^3$ cal /deg is ________	Debye's T-cubed law	Bose Einstein	Fermi Dirac	Maxwell Boltzmann	Debye's T-cubed law
46	___________ law is only a limiting law applicable at high temperature.	Dulongpetits	Einstein	Debye's T-cubed law	Maxwell Boltzmann	Dulongpetits
47	Entropy of _________ gas equation is $S = Nk\alpha + k\beta E + Nk$.	Fermi Dirac	Bose Einstein	Debye’s	Bohr	Bose Einstein
48	Systems having spins of _____________ are called Fermions	½,3/2,5/2	0,1,2,3	0 , ½,3/2	2,4,6	½,3/2,5/2
49	Systems having spins of ___________ are called Bosons	½,3/2,5/2	0,1,2,3	0 , ½,3/2	2,4,6	0,1,2,3
50	A gas at ________ temperature is an example forMaxwellons.	high	low	very low	moderate	high
51	------------- of Bose Einstein gas equation is $S = Nk\alpha + k\beta E + Nk$	Entropy	Enthalpy	Internal energy	Crystal	Entropy
52	In Fermi Dirac statistics only --------- particle can occupy each quantum state	one	two	three	many	one

53	The example for ----------- is proton	Bosons	Fermions	Maxwellons	F.D. statistics	Fermions
54	The electrons obey ---------- and hence paulis exclusion principle only 2 electrons wich occupy each state	Bosons	Fermions	Maxwellons	F.D. statistics	F.D. statistics
55	----------- is used to describe the contribution from lattice vibrations photons	M.B. statistics	F.D. statistics	Maxwellons	B.E. statistics	B.E. statistics
56	------------ statistics must be used to describe the electron contribution to the specific heat	M.B. statistics	F.D. statistics	Maxwellons	B.E. statistics	F.D. statistics
57	**-----------** law describes the electromagnetic radiation emitted by a black body in thermal equilibrium at a definite temperature	Planck	Fermi Dirac	Einstein	Bohr	Planck
58	--------- statistics are often described as the statistics of "distinguishable" classical particles	Bosons	Fermions	Maxwell–Boltzmann	Fermi Dirac	Maxwell–Boltzmann
59	The Maxwell–Boltzmann distribution follows from the ----------- distribution for temperatures well above absolute zero	Planck	Fermi Dirac	Bose-Einstein	Bohr	Bose-Einstein
60	**----------** statistics describes a distribution of particles over energy states in systems consisting of many identical particles that obey the Pauli exclusion principle	Planck	Fermi Dirac	Bose-Einstein	Bohr	Fermi Dirac

Unit V

Einstein's theory and Debye's theories of heat capacities of solids.

Einstein Theory for the Crystalline Solid

Einstein (1907) made the very reasonable assumption that a crystalline lattice can be modeled as an assembly of 3*N* identical, noninteracting harmonic oscillators. In addition, because of the tightly-bound structure of crystalline solids, he presumed that all 3*N* vibrational modes would oscillate at the same fundamental frequency. The molecular partition function for a single harmonic oscillator can be written as

$$Z_{vib} = (1 - e^{-\theta_E/T})^{-1} \quad (1)$$

where $\theta_E = h\nu_E/k$ is the so-called Einstein temperature, which is simply a characteristic vibrational temperature for the crystalline solid. In essence, $\theta_E$is an adjustable parameter that can be used to best match predicted and experimental thermodynamic data for a given metal.

Because the partition function for distinguishable particles is the same as that for indistinguishable particles in the dilute limit, for 3*N* oscillators having the same characteristic temperature,

$$U = 3NkT^2 \left(\frac{\partial \ln Z_{vib}}{\partial T}\right)_V \quad (2)$$

$$C_V = 3Nk \left[\frac{\partial}{\partial T} T^2 \left(\frac{\partial \ln Z_{vib}}{\partial T}\right)\right]_V . \quad (3)$$

$$\frac{u}{RT} = \frac{3\theta_E/T}{e^{\theta_E/T} - 1} \quad (4)$$

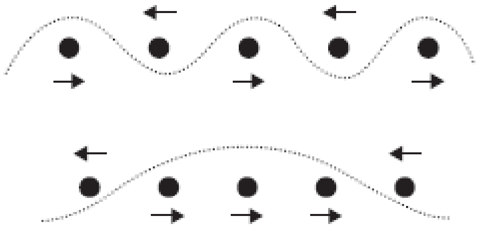
$$\frac{c_v}{R} = \frac{3\,(\theta_E/T)^2\, e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \quad (5)$$

Similarly, for the entropy, the Equation

$$S = 3Nk\left[T\left(\frac{\partial \ln Z_{vib}}{\partial T}\right)_V + \ln Z_{vib}\right], \quad (6)$$

so that from Eqs. (1), (4), and (6) we have, for $3N$ harmonic oscillators,

$$\frac{s}{R} = 3\left[\frac{\theta_E/T}{e^{\theta_E/T}-1} - \ln\left(1-e^{-\theta_E/T}\right)\right] \quad (7)$$



Normal mode structure within a crystallinesolid at higher and lower frequencies.

For comparative purposes, analyzing the limiting behavior forspecific heat at high and low temperatures, as predicted by the Einstein theory. At the hightemperature limit we have, upon invoking series expansions for the exponential terms inEq. (5),

$$\lim_{\theta_E/T\to 0}\frac{c_v}{R} = \frac{3(\theta_E/T)^2\left[1+(\theta_E/T)+\cdots\right]}{\left(1+(\theta_E/T)+\cdots-1\right)^2} \simeq 3$$

so that the expected result has obtained from equipartition theory. Onthe other hand, at the low-temperature limit, we obtain

$$\lim_{\theta_E/T\to\infty}\frac{c_v}{R} = \frac{3(\theta_E/T)^2 e^{\theta_E/T}}{e^{2\theta_E/T}} = 3(\theta_E/T)^2 e^{-\theta_E/T}$$

which obviously disagrees with the observed T^3-dependence near absolute zero. This failure of Einstein theory arises because of a collective coupling among the lattice sites at lower temperatures, now explore by turning to the more successful Debye theory.

Debye Theory for the Crystalline Solid

The energy of an oscillator is proportional to its frequency, an improved statistical model for the crystalline solid at lower temperatures mandates a better understanding of vibrational energy modes at lower frequencies. As for the single atom of a polyatomic gas, the normal frequencies in a crystal describe the concerted harmonic motion of all metallic ions within the lattice structure. At lower frequencies, the resulting wavelengths are long compared to the atomic spacing within the lattice; thus, these frequencies must be determined by analyzing the crystal as a continuous elastic medium. In other words, at lower temperatures, the behavior of a crystalline solid displays features more appropriately described by classical rather than quantum mechanics. At higher frequencies, on the other hand, the wavelength must eventually be limited by the internuclear spacing within the lattice structure, as indicated in Fig. 13.2. The upshot is that neighboring ions tend to move collectively in phase at lower frequencies while ionic pairs gravitate toward out-of-phase motion at higher frequencies.

Based on this distinction between low- and high-frequency behavior, Debye (1912) postulated a continuous distribution of oscillator frequencies, but with a maximum frequency identified with a characteristic internuclear spacing, thus defining the so-called *Debye frequency*. From this postulate, we may write

$$dN = g(\nu)\,d\nu \qquad 0 \le \nu \le \nu_D \quad (1)$$

where$dN$is the number of normal vibrators in the frequency range ν to $\nu + d\nu$, $g(\nu)$ is a frequency distribution function, and $\nu D$is the Debye frequency. Here, we note that $g(\nu)$ is not the usual probability density function, as integration of Eq. (1) over all possible frequencies gives the total number of oscillators for a crystalline solid, so that

$$\int_0^{\nu_D} g(\nu)\,d\nu = 3N. \quad (2)$$

At this point, the required distribution function could be obtained by determining the number of standing acoustic waves produced by thermally excited vibrations within a specified elastic medium. To determine the number of standing electromagnetic waves in a blackbody cavity, From this type of analysis, we find that

$$g(\nu) = \frac{12\pi V}{v_s^3}\nu^2 \quad (3)$$

where*V*represents the volume of the elastic medium and *v*sis the average speed of sound in the metallic crystal. Substituting Eq. (2) into Eq. (1), we obtain

$$g(\nu) = \frac{9N\nu^2}{\nu_D^3} \quad (4)$$

so that the Debye frequency can be related to fundamental crystalline parameters via

$$\nu_D^3 = \frac{3Nv_s^3}{4\pi V} \quad (5)$$

If we now assume that the properties of a crystalline solid can be determined by superimposing the contributions from each normal mode,

$$U = \int_0^{\nu_D} g(\nu)kT^2\left(\frac{\partial \ln Z_{vib}}{\partial T}\right)_V d\nu \quad (6)$$

$$C_V = \int_0^{\nu_D} g(\nu)k\left[\frac{\partial}{\partial T}T^2\left(\frac{\partial \ln Z_{vib}}{\partial T}\right)\right]_V d\nu \quad (7)$$

where, in each case, we have integrated over all possible frequencies after weighing the relevant property per vibrator with its frequency distribution function.
The vibrational partition function for any frequency written as

$$Z_{vib} = (1 - e^{-h\nu/kT})^{-1} \quad (8)$$

so that, substituting Eq. (8) into Eqs. (6) and (5), we obtain

$$U = \int_0^{\nu_D} g(\nu)kT\frac{h\nu/kT}{e^{h\nu/kT} - 1}d\nu \quad (9)$$

$$C_V = \int_0^{\nu_D} g(\nu)k\frac{(h\nu/kT)^2\, e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2}d\nu \qquad (10)$$

Our remaining development will be aided considerably by introducing

$$x = \frac{h\nu}{kT} \qquad x_D = \frac{h\nu_D}{kT} = \frac{\theta_D}{T}$$

where$\theta D$is called the Debye temperature. Given these definitions, Eqs. (9) and (10) become, after substitution from Eq. (4),

$$U = \frac{9NkT}{x_D^3}\int_0^{x_D}\frac{x^3}{e^x-1}dx \qquad (11)$$

$$C_V = \frac{9Nk}{x_D^3}\int_0^{x_D}\frac{x^4e^x}{(e^x-1)^2}dx \qquad (12)$$

Defining the Debye function,

$$D(x_D) = \frac{3}{x_D^3}\int_0^{x_D}\frac{x^3}{e^x-1}dx \qquad (13)$$

and integrating Eq. (13) by parts, we obtain finally the specific internal energy and heat capacity as

$$\frac{u}{RT} = 3D(x_D) \qquad (14)$$

$$\frac{c_v}{R} = 3\left[4D(x_D) - \frac{3x_D}{e^{x_D}-1}\right] \qquad (15)$$

To expedite the evaluation of Eqs. (14) and (15), the Debye function has been numerically integrated and the results tabulated in AppendixM. Note that both the internal energy and specific heat are functions solely of $xD = \theta D/T$. In general, the Debye temperature, θD, is obtained by fitting Eq. (15) to experimental data, although good results can also be had by using Eq. (5) along with the measured speed of sound within a crystalline solid. More significantly, if we explore once again the low-temperature limit for specific heat, we now find

lim

$$\lim_{x_D\to\infty}\frac{c_v}{R}=12\lim_{x_D\to\infty}D(x_D)=12\left[\frac{\pi^4}{5x_D^3}\right]=\frac{12\pi^4}{5}\left(\frac{T}{\theta_D}\right)^3 \quad (16)$$

thus supporting the observed T^3-dependence for $T < 0.05\theta D$.

From Eq. (16) we conclude that the specific heat of a crystalline solid becomes negligible as the temperature approaches absolute zero.

Bose–Einstein statistics

In statistical mechanics, Bose–Einsteinstatistics (or more colloquially B–E statistics) determines the statistical distribution of identical indistinguishablebosons over the energy states in thermal equilibrium.

Fermi-Dirac and Bose–Einstein statistics apply when quantum effects are important and the particles are "indistinguishable". Quantum effects appear if the concentration of particles $(N/V) \geq n_q$. Here n_q is the quantum concentration, for which the interparticle distance is equal to the thermal de Broglie wavelength, so that the wavefunctions of the particles are touching but not overlapping. Fermi–Dirac statistics apply to fermions (particles that obey the Pauli exclusion principle), and Bose–Einstein statistics apply to bosons. As the quantum concentration depends on temperature; most systems at high temperatures obey the classical (Maxwell–Boltzmann) limit unless they have a very high density, as for a white dwarf. Both Fermi–Dirac and Bose–Einstein become Maxwell–Boltzmann statistics at high temperature or at low concentration.

Bosons, unlike fermions, are not subject to the Pauli exclusion principle: an unlimited number of particles may occupy the same state at the same time. This explains why, at low temperatures, bosons can behave very differently from fermions; all the particles will tend to congregate together at the same lowest-energy state, forming what is known as a Bose–Einstein condensate.

B–E statistics was introduced for photons in 1924 by Bose and generalized to atoms by Einstein in 1924-25.

Bose–Einstein Statistics

For each case, deriving an expression for the number of microstates per macrostate, which represents the total number of ways an arbitrary particle distribution can arise when accounting for all possible energy levels. Let us first consider one energy level. The number of ways in which *Nj*bosons in a single energy level, $\varepsilon\ j$, may be distributed among *gj*energy states is equivalent to the number of ways in which *Nj*identical, indistinguishable objects may be arranged in *gj*different containers, with no limitation on the number of objects per container.

$$W_j = \frac{(N_j + g_j - 1)!}{N_j!\,(g_j - 1)!}$$

Because each energy level represents an independent event, the total number of ways of obtaining an arbitrary particle distribution becomes

$$W_{BE} = \prod_j W_j = \prod_j \frac{(N_j + g_j - 1)!}{N_j!\,(g_j - 1)!}$$ (1)

In other words,*WBE*identifies the generic number of microstates per macrostate for Bose–Einstein statistics.

Taking the natural logarithm of Eq. (1), we obtain

$$\ln W_{BE} = \sum_j \{\ln(N_j + g_j)! \; - \; \ln N_j! \; - \ln g_j!\}$$

where we have neglected the unity terms since *gj*_ 1. Applying Stirling's approximation, i.e., ln*N*! = *N*ln*N*− *N* ,we find that

$$\ln W_{BE} = \sum_j \{(N_j + g_j)\ln(N_j + g_j) - N_j \ln N_j - g_j \ln g_j\}$$

or

$$\ln W_{BE} = \sum_j \left\{ N_j \ln \frac{g_j + N_j}{N_j} + g_j \ln \frac{g_j + N_j}{g_j} \right\}.$$ (2)

Fermi–Dirac Statistics

The expression for the number of microstates per macrostate, but this time for fermions. The number of ways in which *Nj*fermions in a single energy level, $\varepsilon\ j$, may be distributed among *gj*energy states is equivalent to the number of ways in which *Nj*identical, indistinguishable objects may be arranged in *gj*different containers, with no more than one object per container.

$$W_j = \frac{g_j!}{N_i!\,(g_i - N_i)!}$$

where the *Nj*! term in the denominator accounts for particle indistinguishability. The total number of ways of obtaining an arbitrary particle distribution then becomes

$$W_{FD} = \prod_j W_j = \prod_j \frac{g_j!}{N_j!\,(g_j - N_j)!} \quad (3)$$

so that *WFD* denotes the generic number of microstates per macrostate for Fermi–Dirac statistics.

Taking the natural logarithm of Eq. (3), we obtain

$$\ln W_{FD} = \sum_j \{\ln g_j! \ - \ln N_j! \ - \ln(g_j - N_j)!\}$$

Applying Stirling'sapproximation ,we find that

$$\ln W_{FD} = \sum_j \{g_j \ln g_j - N_j \ln N_j - \ (g_j - N_j)\ln(g_j - N_j)\}$$

or

$$\ln W_{FD} = \sum_j \left\{N_j \ln \frac{g_j - N_j}{N_j} - g_j \ln \frac{g_j - N_j}{g_j}\right\} \quad (4)$$

The Most Probable Particle Distribution

Equations (2) and (4) combined into one expression for both Bose– Einstein and Fermi–Dirac statistics:

$$\ln W_{\left[\substack{BE \\ FD}\right]} = \sum_j \left\{N_j \ln \frac{g_j \pm N_j}{N_j} \pm g_j \ln \frac{g_j \pm N_j}{g_j}\right\} \quad (1)$$

where the upper sign (+) refers to Bose–Einstein statistics and the lower sign (−) refers to Fermi–Dirac statistics. For simplicity of nomenclature, from here on omit the combined BE-FD subscript; our convention will be that *the upper sign always applies to Bose–Einstein statistics and the lower sign always applies to Fermi–Dirac statistics.*

The most probable particle distributions for Bose–Einstein and Fermi–Dirac statistics can now be determined by maximizing Eq. (1) subject to the two constraints

$$\sum_j N_j = N \quad (2)$$

$$\sum_j N_j \varepsilon_j = E \qquad (3)$$

Equations (2) and (3) reflect the constant (*E*, *V*, *N*) conditions for an isolated system, as required by the M–B method of statistical thermodynamics. Employing the Lagrange method of undetermined multipliers first expand Eq. (1) and then differentiate the result with respect to *Nj*to find the most probable distribution of *Nj* among its allowed energy levels. The step-by-step outcome is

$$\ln W = \sum_j \{N_j \ln(g_j \pm N_j) - N_j \ln N_j \pm \ g_j \ln(g_j \pm N_j) \mp g_j \ln g_j\}$$

$$d \ln W = \sum_j \left\{\ln(g_j \pm N_j) \pm \frac{N_j}{g_j \pm N_j} \ - \ \ln N_j - 1 + \frac{g_j}{g_j \pm N_j}\right\} dN_j$$

$$d \ln W = \sum_j \{\ln(g_j \pm N_j) \ - \ \ln N_j\} \, dN_j, \qquad (4)$$

where*gj*and*ε j* are taken as constants during the differentiation. From quantum mechanics, it turns out that the degeneracy, *gj*, is simply an integer and the level energy, *ε j* , is a function only of the total volume, *V*, which is, constant for an isolated system.

Equations (2) and (3) are now differentiated to account for the imposed constraints during the optimization process. The results are

$$\sum_j dN_j = 0 \qquad \sum_j \varepsilon_j \, dN_j = 0. \qquad (5)$$

Introducing multiplied unknowns into Eqs. (5), we then subtract both expressions from Eq. (4) to guarantee independent values of *Nj*.We thus obtain

$$\sum_j \{\ln(g_j \pm N_j) - \ \ln N_j - \alpha - \beta\varepsilon_j\} \, dN_j = 0 \qquad (6)$$

where the unknowns *α* and *β* are the so-called Lagrange multipliers, and the entire expression is set equal to zero to identify the most probable macrostate.

Eq. (6) can be achieved for all *j* only if

$$\ln \frac{g_j \pm N_j}{N_j} = \alpha + \beta\varepsilon_j$$

Hence, the most probable distribution among energy levels becomes

$$N_j = \frac{g_j}{\exp(\alpha + \beta\varepsilon_j) \mp 1} \qquad (7)$$

Equation (7) thus defines from a molecular viewpoint the specific condition ensuring thermodynamic equilibrium for a macroscopic system of independent particles.

Fermi–Dirac , Bose–Einstein statistics and Maxwell–Boltzmann statistics :

Fermi–Dirac and Bose–Einstein statistics apply when quantum effects are important and the particles are "indistinguishable". Quantum effects appear if the concentration of particles $(N/V) \geq n_q$. Here n_q is the quantum concentration, for which the interparticle distance is equal to the thermal de Broglie wavelength, so the wavefunctions of the particles are touching but not overlapping. Fermi–Dirac statistics apply to fermions (particles that obey the Pauli exclusion principle), and Bose–Einstein statistics apply to bosons. As the quantum concentration depends on temperature; most systems at high temperatures obey the classical (Maxwell–Boltzmann) limit unless they have a very high density, as for a white dwarf. Both Fermi–Dirac and Bose–Einstein become Maxwell–Boltzmann statistics at high temperature or at low concentration.

Maxwell–Boltzmann statistics are often described as the statistics of "distinguishable" classical particles. In other words the configuration of particle A in state 1 and particle B in state 2 is different from the case where particle B is in state 1 and particle A is in state 2. This assumption leads to the proper (Boltzmann) distribution of particles in the energy states, but yields non-physical results for the entropy. This problem disappears when it is realized that all particles are indistinguishable. Both of these distributions approach the Maxwell–Boltzmann distribution in the limit of high temperature and low density, without the need for any assumptions. Maxwell–Boltzmann statistics are particularly useful for studying gases. Fermi–Dirac statistics are most often used for the study of electrons in solids. As such, they form the basis of semiconductor device theory and electronics.

Plank distribution law of black body radiation:

A black body is an idealized physical body that absorbs all electromagnetic radiation falling on it. Because of its perfect absorptivity at all wavelengths, a black body is also the best possible emitter of thermal radiation, which it radiates incandescently in a characteristic, continuous spectrum that depends on the body's temperature. At Earth-ambient, low temperatures this emission is in the infrared region of the electromagnetic spectrum and not visible, and therefore the object appears black, since it does not reflect or emit any visible light.

Black body spectrum (spectral energy density inside a blackbody cavity).

The thermal radiation from a black body is energy converted electrodynamically from the body's of internal thermal energy at any temperature greater than absolute zero. It is called blackbody radiation and has a distribution with a frequency maximum that shifts to higher energies with increasing temperature. As the temperature increases past a few hundred degrees Celsius, black bodies start to emit visible wavelengths, appearing red, orange, yellow, white, and blue with increasing temperature. By the time an object is visually white, it is emitting a substantial fraction as ultraviolet light.

Blackbody emission provides insight into the thermodynamic equilibrium state of the source of a continuous field. According to the equipartition theorem in classical physics, each Fourier mode or degree of freedom should have the same energy when in equilibrium. This approach led to the paradox known as the ultraviolet catastrophe, that there would be an infinite amount of energy in any continuous field.

Explanation

All matter emits electromagnetic radiation when it has a temperature above absolute zero. The radiation represents a conversion of a body's thermal energy into electromagnetic energy, and is therefore called thermal radiation. It is a spontaneous process of radiative distribution of entropy.

Conversely all matter absorbs electromagnetic radiation to some degree. An object that absorbs all radiation falling on it, at all wavelengths, is called a black body. When a black body is at a uniform temperature, its emission has a characteristic frequency distribution that depends on the temperature. Its emission is called blackbody radiation.

The concept of the black body is an idealization, as perfect black bodies do not exist in nature. Graphite is a good approximation, however. Experimentally, blackbody radiation may be established best as the steady state equilibrium radiation in a rigid-walled cavity. A closed box of graphite walls at a constant temperature with a small hole on one side produces a good approximation to ideal blackbody radiation emanating from the opening.

Blackbody radiation becomes a visible glow of light if the temperature of the object is high enough. The Draper point is the temperature at which all solids glow a dim red, about 798 K. At 1000 K, the opening in the oven looks red; at 6000 K, it looks white. No matter how the oven is constructed, or of what material, as long as it is built such that almost all light entering is absorbed, it will be a good approximation to a blackbody, so the spectrum, and therefore color, of the light that comes out will be a function of the cavity temperature temperature alone. A graph of the amount of energy inside the oven per unit volume and per unit frequency interval plotted versus frequency, is called the *blackbody curve*. Different curves are obtained by varying the temperature.

Blackbody radiation is approximated by the radiation from a small hole in a large cavity, a hohlraum, that has reached and is maintained at a constant temperature. (This leads to the *cavity radiation*.) Any light entering the hole would have to reflect off the walls of the cavity multiple times before it escaped, in which process it is nearly certain to be absorbed. Absorption occurs regardless of the wavelength of the radiation entering (as long as it is small compared to the hole). The hole, then, is a close approximation of a theoretical black body and, if the cavity is heated, the spectrum of the hole's radiation (i.e., the amount of light emitted from the hole at each wavelength) will be continuous, and will not depend on the material in the cavity (compare with emission spectrum).

Calculating the blackbody curve was a major challenge in theoretical physics during the late nineteenth century. The problem was solved in 1901 by Max Planck in the formalism now, but its intensity rapidly tends to zero at high frequencies (short wavelengths). For example, a black body at room temperature (300 K) with one square meter of surface area will emit a photon in the visible range (390-750 nm) at an average rate of one photon every 41 seconds, meaning that for most practical purposes, such a black body does not emit in the visible range.

Planck's law states that

where

$I(v,T)\,dv$ is the amount of energy per unit surface area per unit time per unit solid angle emitted in the frequency range between v and $v + dv$ by a black body at temperature T;

h is the Planck constant

c is the speed of light in a vacuum

k is the Boltzmann constant

v is frequency of electromagnetic radiation and

T is the temperature in kelvins.

Planck's law describes the spectral radiance of unpolarizedelectromagnetic radiation at all wavelengths emitted from a black body at absolute temperature$T$. As a function of frequencyν, Planck's law is written as

This function represents the emitted power per unit area of emitting surface in the normal direction, per unit solid angle, per unit frequency. It is a specific radiative intensity. A black body is an ideal surface that absorbs completely, with no reflection or transmission, electromagnetic radiation of any wavelength falling on it. Though perfectly black materials do not exist, such a surface can be accurately approximated by a small opening on a closed cavity, since radiation entering the hole has almost no possibility to escape the cavity without being absorbed by multiple impacts with its walls.

Black bodies are Lambertian objects, which means that the radiance is proportional to the cosine of the viewing angle. Therefore, the spectral radiance of a black body surface viewed from an arbitrary angle θis .

Sometimes, Planck's law is written as for the specific radiative intensity in a cavity in thermodynamic equilibrium; such radiation is isotropic, and homogeneous. Also sometimes, Planck's law is writtenas for spectral energy per unit volume of such cavity radiation. Also sometimes, Planck's Law is written as an expression for power spectral density emitted. The function peaks for . Its integral falls off exponentially in at higher frequencies and polynomially at lower, namely as .

As a function of wavelength λ, Planck's law is written (for unit solid angle) as:

This function peaks for $hc = 4.97\lambda kT$, a factor of 1.76 shorter in wavelength (higher in frequency) than the frequency peak. As for it falls off exponentially for shorter wavelengths and polynomially for longer, with the peculiar difference that the polynomial is . Its peak is the more commonly used one in Wien's displacement law.

The radiance emitted over a frequency range [ν_1,ν_2] or a wavelength range can be obtained by integrating the respective functions.

The order of the integration limits is reversed because increasing frequencies correspond to decreasing wavelengths. The strange difference noted earlier between the polynomials $\nu^2$and at long wavelengths disappears in the integral, which falls off cubically in both frequency and wavelength.

The wavelength is related to the frequency by:

The law is sometimes written in terms of the spectral energy density

which has units of energy per unit volume per unit frequency (joule per cubic meter per hertz). Integrated over frequency, this expression yields the total energy density. The radiation field of a black body may be thought of as a photon gas, in which case this energy density would be one of the thermodynamic parameters of that gas.

The spectral energy density can also be expressed as a function of wavelength:

as shown in the derivation below.

Max Planck originally produced this law in 1900 (published in 1901) in an attempt to improve upon the Wien approximation, which fit the experimental data at short wavelengths (high frequencies) but deviated from it at long wavelengths (low frequencies). Planck found that the above function, Planck's function, fitted the data for all wavelengths remarkably well. In constructing a derivation of this law, he considered the possible ways of distributing electromagnetic energy over the different modes of charged oscillators in matter. Planck's law emerged when he assumed that the energy of these oscillators was limited to a set of discrete, integer multiples of a fundamental unit of energy, *E*, proportional to the oscillation frequency ν:

Planck believed that the quantization applied only to the tiny oscillators that were thought to exist in the walls of the cavity (what we now know to be atoms), and made no assumption that light itself propagates in discrete bundles or packets of energy. Moreover, Planck did not attribute any *physical significance* to this assumption, but rather believed that it was merely a mathematical device that enabled him to derive a single expression for the black body spectrum that matched the empirical data at *all* wavelengths. Planck's formula predicts that a black body will radiate energy at all frequencies, but its intensity rapidly tends to zero at high frequencies (short wavelengths).

Derivation

The Planck's lawdistribution derivation :

Consider a cube of side *L* with conducting walls filled with electromagnetic radiation. Let the cube contain a small particle of black material such as black carbon, so that the radiation will be transduced to black radiation in thermodynamic equilibrium. Planck noted that such a transducer between frequency components is needed because without it the free electromagnetic field in the cavity with perfectly conducting walls cannot exchange energy between frequency components and cannot achieve stable thermodynamic equilibrium. If there is a small hole in one of the walls, the radiation emitted from the hole will be characteristic of a perfect black body. We will first calculate the spectral energy density within the cavity and then determine the spectral radiance of the emitted radiation.

At the walls of the cube, the parallel component of the electric field and the orthogonal component of the magnetic field must vanish. Analogous to the wave function of a particle in a box, one finds that the fields are superpositions of periodic functions. The three wavelengths λ_1,λ_2 and λ_3, in the three directions orthogonal to the walls can be:

where the n_i are integers. For each set of integers n_i there are two linear independent solutions (modes). According to quantum theory, the energy levels of a mode are given by:

The quantum number r can be interpreted as the number of photons in the mode. The two modes for each set of n_i correspond to the two polarization states of the photon which has a spin of 1. Note that for $r = 0$ the energy of the mode is not zero. This vacuum energy of the electromagnetic field is responsible for the Casimir effect. In the following we will calculate the internal energy of the box at temperature T relative to the vacuum energy.

According to statistical mechanics, the probability distribution over the energy levels of a particular mode is given by:

Here

The denominator $Z(\beta)$, is the partition function of a single mode and makes P_r properly normalized:

Here we have implicitly defined

which is the energy of a single photon. As explained here, the average energy in a mode can be expressed in terms of the partition function:

This formula is a special case of the general formula for particles obeying Bose-Einstein statistics. Since there is no restriction on the total number of photons, the chemical potential is zero.

The total energy in the box now follows by summing over all allowed single photon states. This can be done exactly in the thermodynamic limit as L approaches infinity. In this limit, becomes continuous and we can then integrate over this parameter. To calculate the energy in the box in this way, we need to evaluate how many photon states there are in a given energy range. If we write the total number of single photon states with energies between and as , where is the density of states which we'll evaluate in a moment, then we can write:

To calculate the density of states we rewrite equation (1) as follows:

where*n* is the norm of the vector :

For every vector *n* with integer components larger than or equal to zero there are two photon states. This means that the number of photon states in a certain region of n-space is twice the volume of that region. An energy range of corresponds to shell of thickness in n-space. Because the components of have to be positive, this shell spans an octant of a sphere. The number of photon states $g(\varepsilon)\,d\varepsilon$ in an energy range is thus given by:

Inserting this in Eq. (2) gives:

From this equation derives the spectral energy density as a function of frequency *u*(ν,*T*) and as a function of wavelength *u*(λ,*T*):

where:

u(ν,*T*) is known as the black body spectrum. It is a spectral energy density function with units of energy per unit frequency per unit volume.

And:

where

This is also a spectral energy density function with units of energy per unit wavelength per unit volume. Integrals of this type for Bose and Fermi gases can be expressed in terms of polylogarithms. In this case, however, it is possible to calculate the integral in closed form using only elementary functions. Substituting

The integration variable dimensionless giving:

where*J* is given by:

The total electromagnetic energy inside the box is thus given by:

where$V = L^3$ is the volume of the box.

This is not the Stefan-Boltzmann law (which is the total energy *radiated* by a black body – see that article for an explanation); but it can be written more compactly using the Stefan-Boltzmann constant σ, giving

The constant $4\sigma/c$ is sometimes called the radiation constant.

Since the radiation is the same in all directions, and propagates at the speed of light (c), the spectral radiance (energy/time/area/solid angle/frequency) of radiation exiting the small hole is

which yields

It can be converted to an expression for $I'(\lambda,T)$ in wavelength units by substituting ν by c / λ and evaluating

Note that dimensional analysis shows that the unit of steradians, shown in the denominator of left hand side of the equation above, is generated in and carried through the derivation but does not appear in any of the dimensions for any element on the left-hand-side of the equation.

Heat capacities of the electron gas and the heat capacities of metals:

The electron gas is clearly significant as it provides the primary mechanism for the electrical conductivity of metallic crystals. Moreover, the Debye theory for a crystalline solid proves to be inadequate at temperatures below approximately 5 K because adds materially to thermodynamic properties under such conditions. The electrons can be treated as independent particles owing to a roughly constant potential throughout the lattice structure. This relatively constant potential arises from rather long-range forces both among the electrons themselves and also between the electrons and the metallic ions located at the various lattice sites.

Continuing the previous development for a crystalline solid, to determine the thermodynamic properties of its electron gas, particularly the internal energy and specific heat. The only significant energy mode in this case is translation within the conduction band. Consequently, identifying the number of energy states associated with an electron of mass *me* for translational energies between ε and $\varepsilon + d\varepsilon$,

$$D(\varepsilon)\, d\varepsilon = 4\pi \left(\frac{2m_e}{h^2}\right)^{3/2} V\varepsilon^{1/2}\, d\varepsilon \quad (1)$$

we have multiplied the usual density of translational states by a factor of two to account for the intrinsic spin of each electron. Because the Pauli exclusion principle permits only one electron per state, Eq. (1) also represents the number of electrons with translational energies between ε and $\varepsilon + d\varepsilon$at absolute zero. Therefore, the electronic distribution function at any temperature must be

$$N(\varepsilon) = \frac{D(\varepsilon)}{\exp[(\varepsilon - \mu)/kT] + 1} \quad (2)$$

so that the total number of electrons becomes

$$N = \int_0^\infty N(\varepsilon)\, d\varepsilon = \int_0^\infty \frac{D(\varepsilon)\, d\varepsilon}{\exp[(\varepsilon - \mu)/kT] + 1} \quad (3)$$

Substituting Eq. (1) into Eq. (3), and that $0 < \varepsilon < \varepsilon F$,we obtain

$$N = 4\pi \int_0^{\varepsilon_F} \left(\frac{2m_e}{h^2}\right)^{3/2} V\varepsilon^{1/2}\, d\varepsilon \quad (4)$$

at absolute zero. Performing the indicated integration, find from Eq. (4)

$$\varepsilon_F = \mu_0 = \frac{h^2}{8m_e}\left(\frac{3N}{\pi V}\right)^{2/3} \quad (5)$$

so that the Fermi energy has now been shown to depend on the number density of free electrons, which is, affected by the number of valence electrons provided by each atom in the metallic crystal. In general, for the internal energy,

$$U = \int_0^\infty \varepsilon N(\varepsilon)\, d\varepsilon \tag{6}$$

so that, at absolute zero, Eq. (6) becomes

$$U_0 = 4\pi \int_0^{\varepsilon_F} \left(\frac{2m_e}{h^2}\right)^{3/2} V\varepsilon^{3/2}\, d\varepsilon = \frac{3}{5}N\varepsilon_F \tag{7}$$

In other words, as expected, the internal energy cannot be zero, even at absolute zero, owing to the Pauli exclusion principle. Similarly, for the pressure,

$$PV = \frac{2}{3}E_{tr} = \frac{2}{3}U \tag{8}$$

so that, at absolute zero,

$$P_0 = \frac{2}{5}\left(\frac{N\varepsilon_F}{V}\right) \tag{9}$$

Remarkably, Eq. (9) shows that fermions produce positive pressure, even at absolute zero.

To define the Fermi temperature,

$$\theta_F = \frac{\varepsilon_F}{k} \tag{10}$$

which is typically 10^5 K, and thus several orders of magnitude greater than normal metal temperatures. Therefore, despite being evaluated at absolute zero, the internal energy and pressure from Eqs. (7) and (9), respectively. Moreover, even at substantial temperatures, $T << \theta F$and thus thermodynamic properties for an electron gas should differ insignificantly from those evaluated at absolute zero. On this basis, determine the chemical potential at higher temperatures by manipulating Eq. (2) via a series expansion for μ about $\mu 0$. Similarly, the internal energy can be determined by solving Eq. (6) via the implementation of a Taylor expansion about$U0$.

Fermi–Dirac integrals both below and above the Fermi energy, eventually show that (Davidson, 1962)

$$\mu = \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{\varepsilon_F} \right)^2 + \cdots \right] \quad (11)$$

$$U = U_0 \left[1 + \frac{5\pi^2}{12} \left(\frac{kT}{\varepsilon_F} \right)^2 + \cdots \right] \quad (12)$$

Hence, the chemical potential decreases and the internal energy increases, but ever so slightly compared to their respective values at absolute zero. The chemical potential drops because the energy level at which half the quantum states become filled declines at greater temperatures, as electrons move to higher energy states.

This movement to higher energy levels also causes, an increase in the internal energy of the electron gas.

From Eqs. (7) and (12) we obtain

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} = \frac{\pi^2}{2} Nk \left(\frac{kT}{\varepsilon_F} \right)$$

so that the specific heat contributed by the electron gas becomes

$$\frac{c_v}{R} = \frac{\pi^2}{2} \left(\frac{T}{\theta_F} \right) \quad (13)$$

Eq. (13) implies that only electrons near the Fermi energy become sufficiently agitated thermally to contribute to the specific heat. Moreover, given typical values of the Fermi temperature, this contribution is not 1.5*R*, as for the ideal gas, but on the order of $10^{-2}R$. For electronic contributions of this magnitude are negligible, except as compared to the the lattice structure at very low temperatures.

The electron gas to solid-state physics remains otherwise quite significant across the entire temperature range, especially with respect to modeling the thermionic properties of metals and also their electrical and thermal conductivities.

Negative Absolute Temperature

The property of a thermodynamical system which satisfies certain conditions and whose thermodynamically defined absolute temperature is negative. The essential requirements for a thermodynamical system to be capable of negative temperature are: (1) the elements of the thermodynamical system must be in thermodynamical equilibrium among themselves in order for the system to be described by a temperature at all; (2) there must be an upper limit to the possible energy of the allowed states of the system; and (3) the system must be thermally isolated from all systems which do not satisfy both requirements (1) and (2); that is, the internal thermal equilibrium time among the elements of the system must be short compared to the time during which appreciable energy is lost to or gained from other systems.

The second condition must be satisfied if negative temperatures are to be achieved with a finite energy. Most systems do not satisfy this condition; for example, there is no upper limit to the possible kinetic energy of a gas molecule. Systems of interacting nuclear spins, however, have the characteristic that under suitable circumstances they can satisfy all three of the conditions, in which case the nuclear spin system can be at negative absolute temperature.

The transition between positive and negative temperatures is through infinite temperature, not absolute zero; negative absolute temperatures should therefore not be thought of as colder than absolute zero, but as hotter than infinite temperature. An effective quantity introduced for the description of nonequilibrium states of quantum systems. A system is in a negative temperature state when high energy levels are more populated than low energy levels. The probability for a system in an equilibrium state to be on the level is determined by the equation.

Here, $£_i$, are the energy levels of the system, *k* is the Boltzmann constant, and *T* is the absolute temperature, which characterizes the mean energy of the equilibrium system $U = \Sigma W_n £_n$ Equation (1) indicates that the low energy levels are more populated by particles than the high energy levels. If external influences cause the system to enter a nonequilibrium state characterized by a greater population of the higher levels than the lower levels, it is formally possible to make use of equation (1) by setting $T< 0$. The concept of negtive temperature is applicable only to quantum systems that contain a finite number of levels.

The absolute temperature T is defined in thermodynamics through its reciprocal *l/T*, which is equal to the derivative of the entropy S with respect to the mean energy of the system, the remaining parameters x being kept constant:

Equation (2) indicates that the negative temperature implies a decrease of entropy with increasing mean energy. Negative temperature, however, is introduced for the description of nonequilibrium states, to which the laws of equilibrium thermodynamics are applicable only conditionally.

An example of a system with negative temperature is the system of nuclear spins in a crystal located in a magnetic field when the spins interact very weakly with the thermal lattice vibrations—that is, a system practically isolated from thermal motion. The time required for the attainment of thermal equilibrium of the spins with the lattice is of the order of several tens of minutes. During this time, the system of nuclear spins may be in a state with negative temperature, a state it entered under external influences.

In a narrower sense, negative temperature is a characteristic of the degree of inversion of the populations of two selected energy levels in a quantum system. In the case of thermodynamic equilibrium, the relation between the populations N_1 and N_2 of the levels $£_1$ and $£_2$ ($£_1< £_2$), that is, the mean numbers of particles in these states, is given by the Boltzmann equation:

where$T$ is the absolute temperature of the substance. Equation (3) implies that $N_2<N_1$. Let us suppose the equilibrium of the system is disturbed, for example, by irradiation of the system with monochromatic electromagnetic radiation, whose frequency is close to the frequency of the

transition between the levels $\omega_{21} = (£_2 — £_1)$ and is different from the frequencies of other transitions. It is then possible to attain a state in which the population of the upper level is greater than that of the lower level: $N_2 > N_1$. If the Boltzmann equation is conditionally applied to such a nonequilibrium state, negative temperature can be introduced with respect to the pair of energy levels $£_1$ and $£_2$ in accordance with the equation.

System at negative absolute temperature

If more particles are at the upper level than at the lower one, absolute temperature of a system is negative temperature of a system is negative.

As soon as the high energy level is populated more that the low energy one, we have negative absolute temperature.

A state of matter to which negative absolute temperature can be attributed has *more* energy than the states at usual temperatures, because more particles are at high energy level than at low energy level. Thus one has to addenergy to get negative absolute temperature. It has been emphasized that such states cannot be reached by adding heat to a body.

Reg. No. : ----------------------------- **[18CHP302]**

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-21
(For the candidates admitted from 2018 & onwards)
M.Sc. DEGREE EXAMINATION, AUGUST 2018
Third Semester
Chemistry
INTERNAL TEST - I
PHYSICAL CHEMISTRY-III (Thermodynamics)

DATE: 28/8/2019 & SESSION : FN **SUBJECT CODE: 18CHP302**
TIME: 2 HRS **TOTAL: 50 MARKS**

ANSWER ALL THE QUESTIONS

1. Thermodynamics is applicable to

   a) microscopic systems only b) macroscopic systems only c) homogeneous systems only d) heterogeneous systems only.

2. $\Delta E = q - w$ is the mathematical relation for the __________

   a) first law of thermodynamics b) second law of thermodynamics

   c) third law of thermodynamics d) zeroth's law

3. ΔH is +ve for ___________

   a) endothermic process b) exothermic process c) exoergic process d) endoergic process

4. For an endothermic reaction_____________

   a) ΔH is –ve b) ΔH is +ve c) ΔE is –ve d) ΔH is zero

5. The enthalpy of a system is defined by the relation __________

   a) $H=E+PV$ b) $H=E-PV$ c) $E=H+PV$ d) $PV+E-H$

6. The amount of heat required to raise the temperature of one mole of the substance by 1 K is called

   a) heat capacity b) molar heat capacity c) molar capacity d) molar heat

7. A _________ is one which cannot transfer matter but transfer heat, work and radiations to and from its surroundings.

   a) an isolated system b) an open system c) a homogeneous system d) a closed system

8. Every substance has a finite entropy which may become zero at absolute zero of temperature is __________ of thermodynamics.

a) second law b) third law c) first law d) zeroth law.

9. The residual entropy of hydrogen is due to the existence of __________ form of hydrogen in different quantum state.

a) ortho b) para c) meta d) combination.

10. At low pressure, Fugacity becomes

a) equal to pressure b) greater than pressure c) less than pressure d) not equal to pressure

11. The activity of the real gas

a) $\alpha = P$ b) $\alpha \geq P$ c) $\alpha \leq P$ d) $\alpha < P$

12. In the limit $T \to 0$, $S = 0$ which represents ______

a) first law of thermodynamics b) second law of thermodynamics

c) third law of thermodynamics d) zeroth's law

13. Gibbs-Duhem equation is

a) $n_1 d\mu_1 + n_2 d\mu_2 = 0$ b) $n_1\mu_1 + n_2\mu_2 = 0$ c) $dn_1 \mu_1 + dn_2 \mu_2 = 0$ d) $n_1 \mu_1 + n_2 \mu_2 = 1$

14. The residual entropy of ________ is 6.23 $JK^{-1} mol^{-1}$.

a) hydrogen b) oxygen c) nitrogen d) sulphur

15. The number of _________ degrees of freedom in linear molecule is 3N-5

a) rotational b) vibrational c) translational d) electronic

16. Planck proposed the relationship between the entropy of a system and the thermodynamic probability is given by the equation _______

a) S=klnw b) -S=klnw c) S= -klnw d) S=klnT

17. According to Debye theory in the limit $T \to 0$ Cv of a monoatomic crystal is proportional to_________

a) T b) T^2 c) T^3 d) T^4

18. The Nernst heat theorem is _______

a) $\Delta G = \Delta H$ b) $\Delta G \geq \Delta H$ c) $\Delta G \leq \Delta H$ d) $\Delta G \neq \Delta H$

19. The ideal gas equation for one mole of the substance

a) PV = nRT b) PV = RT c) PV ≥ RT d) PV ≥ nRT

20. The number of vibrational degrees of freedom in non- linear molecule is_______

a) 3N-5 b) 3N-4 c) 3N-6 d) 3N-7

Part B **(3x2=6 Marks)**

Answer All the Questions

21. What is Partial molar properties?

22. Write briefly about chemical potential.

23. Give the physical significance of fugacity.

Part C **(3x8=24 Marks)**

Answer All the Questions

24. a) Explain how the fugacity of a gas may be determined by a graphical method.

(Or)

b) Derive the expression for the vapour pressure method for the determination of activity of the solvent and solute.

25. a) write notes on Nernst and third law of thermodynamics.

(Or)

b) What is chemical potential? Derive the Gibbs-Duhem equation.

26. a) Evaluate average speed , Root mean square speed and Most probable speed

(Or)

b) What is meant by fugacity? Explain the variation of fugacity with temperature.

Reg. No. : ------------------- **[18CHP 302]**

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-21
(For the candidates admitted from 2018& onwards)
M.Sc. DEGREE EXAMINATION, SEPTEMBER 2019
Third Semester
Chemistry
INTERNAL TEST - II
PHYSICAL CHEMISTRY-III (Thermodynamics)

Time: 2 Hours **Maximum:50 marks**

PART- A **(20 x 1 = 20 Marks)**
Answer All the Questions

1. The zero-point energy of an S.H.O. whose vibrational frequency is ν, is given by ________

a) hν b) hν/3 c) hν/2 d) hν/4

2. The rotational contribution to Cv for a polyatomic molecule in linear molecule is ________

a) Cv (rot)=R b) Cv (rot)=3/2 R c) Cv (rot)=3R d) Cv (rot)=5R

3. The equation for monoatomic gas is ________

a) Cv=3/2 R b) Cv=R c) Cv=5/2 R d) Cv=5R

4. Planck proposed the relationship between the entropy of a system and the thermodynamic probability is given by the equation _______

a) S=klnw b) -S=klnw c) S= -klnw d) S=klnT

5. The total partition function equation is _________

a) $q = q_{tr}.q_{rot}.q_{vib}..q_{ele}$ b) $q = q_{tr}.q_{ele}$ c) $q = q_{tr}.q_{vib}$ d) $q = q_{rot}.q_{vib}$

6. The units of molecular partition functionare ________

a) cm^{-1} b) s^{-1} c) $JK^{-1}mol^{-1}$ d) dimensionless

7. If Q is the molar (canonical) partition function, then the work function A, is given by

a) A=kTlnQ b) A= -kTln Q c) A=lnQ/kT d) A=kT/lnQ

8. Which of the following are fermions:

a) ^{2}D b) proton c) a gas at high temperature d) $^{4}He_2$

9. B.E. statistics wave functions is _______

a) symmetric b) antisymmetric c) restricted d) only even values

10. The value of 1 belongs to _________

a) average speed b) average square speed

c) most probable speed d) root mean square speed

11. If spins are antiparallel in rotational partition function to para hydrogen then it has__________

a) even quantum number b) odd quantum number

c) odd and even quantum number d) fractional values

12. If spins are parallel in ortho hydrogen it has even quantum number then it is said to be ___________

a) symmetric b) antisymmetric c) rotational energy d) vibrational energy

13. The translational motion for H_{tr} is _________

a) 5/2RT b) 3/2R c) 5/2R d) R

14. The number of vibrational degrees of freedom in non- linear molecule is_______

a) 3 N-5 b) 3 N-4 c) 3 N-6 d) 3 N-7

15. $\sqrt{8RT/\pi M}$ equation of Maxwell distribution law is _________

a) most probable speed b) average square speed

c) average speed d) root mean square speed

16. The equation of ln N! =N ln N –N __________ represents?

a) Stirlings approximation b) partition function

c) equipartition law d) Maxwell Boltzmann distribution law

17. The equation for the evaluation of β in M.B.distribution law is ________

a) $\beta = 1/kT$ b) $\beta = -1/kT$ c) $\beta = kT$ d) $\beta = 2/kT$

18. A single particle is referred to as a ______________

a) system b) assembly c) ensemble d) canonical ensemble

19. In ________ statistics only one particle can occupy each quantum state.

a) Fermi Dirac b) Bose Einstein c) Debye’s d) Bohr

20. ____________assumed that all the particles in a crystal vibrate with same frequency

a) Debye’s b) Fermi Dirac c) Einstein d) Bohr

Part B **(3x2 = 6 Marks)**

Answer All the Questions

21. Write the assumption of Boltzmannons and Fermions.
22. What is a Canonical ensemble?
23. Comment on thermodynamic probability.

Part C **(3x8 = 24 Marks)**

Answer All the Questions

24. a) i)Explain Stirling's approximation.

    ii) Calculate the number of ways in which 16 distinguishable balls can be distributed in to 4 boxes.Show that the first box contains 2 balls and second boxes 6 balls and third boxes 6 balls and fourth boxes 2 balls.

(Or)

b) Derive the equation for Maxwell-Boltzmann distribution law.

25. a) Derive an equation for translational partition function.

(Or)

b) Derive an expression for vibrational partition function.

26. a) What is Bose-Einstein distribution law? Derive the equation for it.

(Or)

b) Explain the Einstein's theories of heat capacities of solids.

Reg. No. : ----------------------------- **[18CHP302]**

KARPAGAM ACADEMY OF HIGHER EDUCATION

COIMBATORE-21

(For the candidates admitted from 2018 & onwards)

M.Sc. DEGREE EXAMINATION, AUGUST 2018

Third Semester

Chemistry

INTERNAL TEST - I

PHYSICAL CHEMISTRY-III (Thermodynamics)

DATE: 28/8/2019 & SESSION : FN **SUBJECT CODE: 18CHP302**

TIME: 2 HRS **TOTAL: 50 MARKS**

ANSWER ALL THE QUESTIONS

1. b) macroscopic systems only
2. a) first law of thermodynamics
3. a) endothermic process
4. b) ΔH is +ve
5. $H=E+PV$
6. b) molar heat capacity
7. d) a closed system
8. b) third law
9. a) ortho
10. c) less than pressure
11. a) $\alpha = P$
12. c) third law of thermodynamics
13. a) $n1\, d\mu1 + n2\, d\mu2 = 0$
14. a) hydrogen
15. b) vibrational
16. a) $S=k\ln w$
17. b) $T2$

18. a) $\Delta G = \Delta H$
19. b) $PV = RT$
20. c) 3N-6

Part B **(3x2=6 Marks)**

Answer All the Questions

21. A partial molar property is a thermodynamic quantity which indicates how an extensive property of a solution or mixture varies with changes in the molar composition of the mixture at constant temperature and pressure, or for constant values of the natural variables of the extensive property considered.

22. Gibbs definition, any chemical element or combination of elements in given proportions may be considered a substance, whether capable or not of existing by itself as a homogeneous body. Chemical potential is also referred to as partial molar Gibbs energy. Chemical potential is measured in units of energy/particle or, equivalently, energy/mole.

23. Fugacity is the effective pressure for a non-ideal gas. The pressures of an ideal gas and a real gas are equivalent when the chemical potential is the same. The equation that relates the non-ideal to the ideal gas pressure is:

$$\Phi = f / P$$

In this equation, f represents fugacity, P is the pressure for an ideal gas, and Φ is the fugacity coefficient. For an ideal gas, the fugacity coefficient is 1.

Part C **(3x8=24 Marks)**

Answer All the Questions

24.

The Gibbs free energy depends on pressure as well as on temperature. The pressure dependence of the Gibbs free energy in a closed system is given by the combined first and second laws and the definition of Gibbs free energy as,

$$dG = -SdT + Vdp \quad \longrightarrow 1$$

If we hold temperature constant and vary only the pressure. Equation 1 for integration from pressure p_1 to p_2 as follows:

$\longrightarrow$ 2

Then

$\longrightarrow$ 3

or

. $\longrightarrow$ 4

Equation 4 is general and applies to all isotropic substance: solids, liquids, ideal gases, and real gases.

(or)

Activity is a measure of the effective concentration of a species under non-ideal (e.g., concentrated) conditions. This determines the real chemical potential for a real solution rather than an ideal one.

Activities and concentrations can both be used to calculate equilibrium constants and reaction rates. However, most of the time we use concentration even though activity is also a measure of composition, similar to concentration. It is satisfactory to use concentration for diluted solutions, but when you are dealing with more concentrated solutions, the difference in the observed concentration and the calculated concentration in equilibrium increases. This is the reason that the activity was initially created.

$$a=e\mu-\mu o /RT$$

where a=Activity, μ is chemical potential (dependent on standard state) which is Gibbs Energy per mole, μ0 is the standard chemical potential, R is the gas constant, T is the absolute Temperature.

The activity of a species i, denoted ai, is defined as:

where μi is the chemical potential of the species under the conditions of interest, μoi is the chemical potential of that species in the chosen standard state, R is the gas constant and T is the thermodynamic temperature. This definition can also be written in terms of the chemical potential:

The activity will depend on any factor that alters the chemical potential. These include temperature, pressure, chemical environment etc. The activity also depends on the choice of standard state, as it describes the difference between an actual chemical potential and a standard chemical potential. In principle, the choice of standard state is arbitrary, although there are certain conventional standard states which are usually used .

25. a) write notes on Nernst and third law of thermodynamics.

The third law of thermodynamics is a statistical law of nature regarding entropy and the impossibility of reaching absolute zero, the null point of the temperature scale. As a system approaches absolute zero, all processes cease and the entropy of the system approaches a minimum value.

This minimum value, the residual entropy, is not necessarily zero, although it is always zero for a perfect crystal in which there is only one possible ground state.

The third law of thermodynamics states that the entropy of a system at absolute zero is a well-defined constant. This is because a system at zero temperature exists in its ground state, so that its entropy is determined only by the degeneracy of the ground state. It means that "it is impossible by any procedure, no matter how idealised, to reduce any system to the absolute zero of temperature in a finite number of operations".

The third law of thermodynamics as stated by Gilbert N. Lewis and Merle Randall:

> If the entropy of each element in some (perfect) crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy; but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances.

Nernst heat theorem

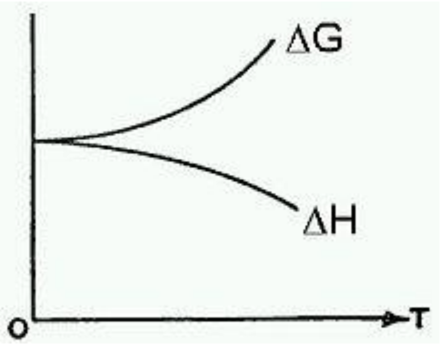
The Nernst heat theorem was formulated by Walther Nernst and was used in the development of the third law of thermodynamics.

The theorem

The Nernst heat theorem says that as absolute zero is approached, the entropy change ΔS for a chemical or physical transformation approaches 0. This can be expressed mathematically as follow

$$\lim_{T\to 0} \Delta S = 0$$

The above equation is a modern statement of the theorem. Nernst often used a form that avoided the concept of entropy.



Graph of energies at low temperatures

The theorem is to start with the definition of the Gibbs free energy (G), $G = H - TS$, where H stands for enthalpy. For a change from reactants to products at constant temperature and pressure the equation becomes $\Delta G = \Delta H - T\Delta S$.

In the limit of $T = 0$ the equation reduces to just $\Delta G = \Delta H$, which is supported by experimental data. From thermodynamics that the slope of the ΔG curve is -ΔS. Since the slope shown here reaches the horizontal limit of 0 as $T \rightarrow 0$ then the implication is that $\Delta S \rightarrow 0$, which is the Nernst heat theorem.

The significance of the Nernst heat theorem is that it was later used by Max Planck to give the third law of thermodynamics, which is that the entropy of all pure, perfectly crystalline homogeneous materials is 0 at absolute zero.

Or

b) What is chemical potential? Derive the Gibbs-Duhem equation.

There are several Gibbs-Duhem equations, although the name is most commonly associated with just one of them. They refer to the *properties of fluid (gas or liquid) mixtures* at fixed pressure and temperature. The equations all have the same form, namely:

$$\sum n_i d\bar{\bar{f}}_i = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

where $\bar{\bar{f}}_i$ is a partial molar quantity for component i, n_i is the number of moles of i present in the mixture and the summation is over all components present in the mixture, $\bar{\bar{f}}_i$ can be any partial molar quantity, volume, enthalpy, entropy etc., but the one of greatest utility is the partial molar Gibbs free energy, usually called the **Chemical Potential**, μ, defined by:

$$\mu_i = (\partial G / \partial n_i)_{P,T,n_j} \quad \ldots\ldots\ldots..(2)$$

where G is the Gibbs Free Energy and n_j in the constraint list indicates that all amounts of substance are to be held fixed, except for n_i, when performing the differentiation.
The Gibbs-Duhem equation for this partial molar quantity, and the one most normally associated with the name, is then:

$$\sum n_i d\mu_i = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

This equation shows that the chemical potentials in a mixture are not all independent and that there is a constraint equation which they must satisfy.

26 Maxwell–Boltzmann distribution

The Maxwell–Boltzmann distribution describes particle speeds in gases, where the particles do not constantly interact with each other but move freely between short collisions. It describes the probability of a particle's speed (the magnitude of its velocity vector) being near a given value as a function of the temperature of the system, the mass of the particle, and that speed value. This probability distribution is named after James Clerk Maxwell and Ludwig Boltzmann.

The Maxwell–Boltzmann distribution is usually for the distribution of molecular speeds, velocities, momenta, and magnitude of the momenta of the molecules, each of which will have a different probability distribution function. "Maxwell–Boltzmann distribution" refer to the distribution of speed. This distribution can be thought of as the magnitude of a 3-dimensional vector whose components are independent and normally distributed with mean 0 and standard deviation$a$. If X_i are distributed as , then

is distributed as a Maxwell–Boltzmann distribution with parameter a. Apart from the scale parameter a, the distribution is identical to the chi distribution with 3 degrees of freedom.

The Maxwell–Boltzmann distribution applies to ideal gases close to thermodynamic equilibrium, negligible quantum effects, and non-relativistic speeds. It forms the basis of the kinetic theory of gases, which explains many fundamental gas properties, including pressure and diffusion.

Derivation

The derivation by Maxwell assumed all three directions would behave in the same fashion, but a later derivation by Boltzmann dropped this assumption using kinetic theory. The Maxwell–Boltzmann distribution can be derived from the Boltzmann distribution for energies.

whereN_i is the number of molecules at equilibrium temperature T, in a state i which has energy E_i and degeneracy g_i, N is the total number of molecules in the system and k is the Boltzmann constant. (Sometimes the above equation is written without the degeneracy factor g_i. In this case the index i will specify an individual state, rather than a set of g_i states having the same energy E_i.) Because velocity and speed are related to energy, Equation 1 can be used to derive relationships between temperature and the speeds of molecules in a gas. The denominator in this equation is known as the canonical partition function.

For the case of an "ideal gas" consisting of non-interacting atoms in the ground state, all energy is in the form of kinetic energy, and g_i is constant for all i. The relationship between kinetic energy and momentum for massive particles is

wherep^2 is the square of the momentum vector $\mathbf{p} = [p_x, p_y, p_z]$. Rewrite Equation 1 as:

where$Z$ is the partition function, corresponding to the denominator in Equation 1. Here m is the molecular mass of the gas, T is the thermodynamic temperature and k is the Boltzmann constant. This distribution of $N_{\mathbf{i}}/N$ is proportional to the probability density function$f_{\mathbf{p}}$ for finding a molecule with these values of momentum components, so:

The normalizing constant$c$, can be determined by recognizing that the probability of a molecule having *any* momentum must be 1. Therefore the integral of equation 4 over allp_x, p_y, and p_z must be 1.

It can be shown that:

Substituting Equation 5 into Equation 4 gives:

The distribution is the product of three independent normally distributed variables p_x, p_y, and p_z, with variance mkT.Additionally,the magnitude of momentum will be distributed as a Maxwell–Boltzmann distribution, with $a= \sqrt{mkT}$The Maxwell–Boltzmann distribution for the momentum (or equally for the velocities) can be obtained using the H-theorem at equilibrium within the kinetic theory.

Or

the fugacity

For a given temperature T, the fugacity *f* satisfies the following differential relation:

where G is the Gibbs free energy, R is the gas constant, v is the fluid's molar volume, and f_0 is a reference fugacity which is generally taken as 1 bar. For an ideal gas, when $f = P$, this equation reduces to the ideal gas law.

$$\mu_i = \mu_i + RT \ln f_i \rightarrow 1$$

Dividing the equation throughout by T

$$\mu_i / T = \mu_i / T + R \ln f_i$$

$$R \ln f_i = \mu_i / T - \mu_i / T \rightarrow 2$$

We know that

$[\partial(\mu_i / T) / \partial T)]_{P,N} = -H_i / T^2 \rightarrow 3$

Differentiating equation 2 with respect to T at constant P and N

$R.\partial (\ln f_i) / \partial T = \partial(\mu_i / T) / \partial T - \partial(\mu_i / T) / \partial T$

$\partial (\ln f_i) / \partial T = H_i - H_i / RT^2$.

Reg. No. : ------------------- [18CHP 302]

KARPAGAM ACADEMY OF HIGHER EDUCATION

COIMBATORE-21

(For the candidates admitted from 2018& onwards)

M.Sc. DEGREE EXAMINATION, SEPTEMBER 2019

Third Semester

Chemistry

INTERNAL TEST - II

PHYSICAL CHEMISTRY-III (Thermodynamics)

Time: 2 Hours Maximum:50 marks

PART- A (20 x 1 = 20 Marks)

Answer All the Questions

c) hν/2

a) Cv (rot)=R

Cv=3/2 R

a) S=klnw

a) q = qtr.qrot.qvib..qele

d) dimensionless

b) A= -kTln Q

b) proton

a) symmetric

d) root mean square speed

b) odd quantum number

a) symmetric

a) 5/2RT

a) 3 N-5

b) average speed

a) Stirlings approximation

a) β = 1/kT

a) system

a) Fermi Dirac

c) Einstein

Part B (3x2 = 6 Marks)

Answer All the Questions

The Maxwell–Boltzmann distribution describes particle speeds in gases, where the particles do not constantly interact with each other but move freely between short collisions. It describes the probability of a particle's speed (the magnitude of its velocity vector) being near a given value as a function of the temperature of the system, the mass of the particle, and that speed value. This probability distribution is named after James Clerk Maxwell and Ludwig Boltzmann.
In statistical mechanics, a canonical ensemble is the statistical ensemble that represents the possible states of a mechanical system in thermal equilibrium with a heat bath at a fixed temperature.
Comment on thermodynamic probability.
Thermodynamic Probability. the number of processes by which the state of a physical system can be realized. In thermodynamics a system is characterized by specific values of density, pressure, temperature, and other measurable quantities

Part C (3x8 = 24 Marks)

Answer All the Questions

a) i)Explain Stirling’s approximation.

Stirling's approximation gives an approximate value for the factorial function $n!$ or the gamma function $\Gamma(n)$ for $n \gg 1$. The approximation can most simply be derived for n an integer by approximating the sum over the terms of the factorial with an integral, so that

$$\ln n! = \ln 1 + \ln 2 + \ldots + \ln n \qquad (1)$$

$$= \sum_{k=1}^{n} \ln k \qquad (2)$$

$$\approx \int_1^n \ln x \, d\,x \qquad (3)$$

$$= [x \ln x - x]_1^n \qquad (4)$$

$$= n \ln n - n + 1 \qquad (5)$$

$$\approx n \ln n - n.$$

(Or)

b) Derive the equation for Maxwell-Boltzmann distribution law.

The derivation by Maxwell assumed all three directions would behave in the same fashion, but a later derivation by Boltzmann dropped this assumption using kinetic theory. The Maxwell–Boltzmann distribution can be derived from the Boltzmann distribution for energies.

$$\frac{N_i}{N} = \frac{g_i \exp\left(-E_i/kT\right)}{\sum_j g_j \exp\left(-E_j/kT\right)} \qquad (1)$$

whereN_i is the number of molecules at equilibrium temperature T, in a state i which has energy E_i and degeneracy g_i, N is the total number of molecules in the system and k is the Boltzmann constant. (Sometimes the above equation is written without the degeneracy factor g_i. In this case the index i will specify an individual state, rather than a set of g_i states having the same energy E_i.) Because velocity and speed are related to energy, Equation 1 can be used to derive relationships between temperature and the speeds of molecules in a gas. The denominator in this equation is known as the canonical partition function.

For the case of an "ideal gas" consisting of non-interacting atoms in the ground state, all energy is in the form of kinetic energy, and g_i is constant for all i. The relationship between kinetic energy and momentum for massive particles is

wherep^2 is the square of the momentum vector **p** = [p_x, p_y, p_z]. Rewrite Equation 1 as:

where$Z$ is the partition function, corresponding to the denominator in Equation 1. Here m is the molecular mass of the gas, T is the thermodynamic temperature and k is the Boltzmann constant. This distribution of $N_\mathbf{i}/N$ is proportional to the probability density function$f_\mathbf{p}$ for finding a molecule with these values of momentum components, so:

The normalizing constant$c$, can be determined by recognizing that the probability of a molecule having *any* momentum must be 1. Therefore the integral of equation 4 over allp_x, p_y, and p_z must be 1.

It can be shown that:

Substituting Equation 5 into Equation 4 gives:

The distribution is the product of three independent normally distributed variables p_x, p_y, and p_z, with variance mkT.Additionally,the magnitude of momentum will be distributed as a Maxwell–Boltzmann distribution, with a= √mkTThe Maxwell–Boltzmann distribution for the momentum (or equally for the velocities) can be obtained using the H-theorem at equilibrium within the kinetic theory.

a) Derive an equation for translational partition function.

The translational part of the motion of a molecule by particle-in-a-box states. The energy of a particle in a one-dimensional of length, *l*, box depends on one quantum number, *n*, which can be 1, 2, 3, . . . up to infinity. The equation for the quantized energy is,

$$E_n = \frac{h^2 n^2}{8ml^2},$$

where*h* is Planck's constant and *m* is the mass of one molecule.

The partition function for this system is,

$$q = \sum_n e^{-\beta \frac{h^2 n^2}{8ml^2}}.$$

The summation cannot be performed in closed form but it can be approximated by an integral to high accuracy,

$$q = \int_0^\infty e^{-\beta \frac{h^2 n^2}{8ml^2}} dn.$$

This integral can be evaluated and gives

$$q \approx \left(\frac{2\pi mkt}{h^2}\right)^{\frac{1}{2}} l.$$

Translational Motion In Three Dimensions

Translational motion in three dimensions there are three quantum numbers, one for each direction, n_x, n_y, and n_z, and the energy is

$$E_{n_x n_y n_z} = \frac{h^2}{8ml^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

The translational partition function in three dimensions is a three−fold summation

$$q_{\text{trans}} = \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{-\beta \frac{h^2}{8ml^2}\left(n_x^2 + n_y^2 + n_z^2\right)}.$$

This equationcan be written as

$$q_{\text{trans}} = \left(\sum_{n} e^{-\beta \frac{h^2 n^2}{8ml^2}} \right)^3.$$

Since already approximated the summation in Equation by an integral immediately write

$$q_{\text{trans}} \approx \left(\frac{2\pi mkt}{h^2} \right)^{\frac{3}{2}} V$$

where let $l^3 = V$

The rotational energy of a linear molecule (neglecting such things as centrifugal distortion) is given by $BJ(J+1)$ and each J level is $2J+1$ degenerate. The rotational partition function is easy to write,

$$q_{\text{rot}} = \sum_{J} (2J+1) e^{-\beta BJ(J+1)}.$$

If $\beta B << 1$ (this is the high temperature limit) the summation can be approximated by an integral to give

$$q_{\text{rot}} \approx \frac{1}{\beta B} = \frac{kT}{B}.$$

For a heteronuclear diatomic molecule (or an unsymmetrical one, like HCN) have to rotate the molecule all the way around 360° to bring it back to the same "state." For a homonuclear diatomic molecule (or a symmetrical one, such as CO_2) it comes back to the same "state" after only 180° rotation. So an asymmetric molecule, in going around 360° has only passed through one "state," while a symmetric molecule has passed through two "states" in a 360° rotation.

$$q_{\mathrm{rot}} \approx \frac{kT}{B\sigma},$$

whereσ is called the symmetry number. σ is the number of ways the molecule can be oriented which are indistinguishable from each other. For HCl, $\sigma = 1$; and for Cl_2, $\sigma = 2$ (as long as both Cl atoms are the same isotope).

The "characteristic rotational temperature," Θ_R, as

$$\Theta_{\mathrm{R}} = \frac{B}{k},$$

so that the rotational partition function can be written,

$$q_{\mathrm{rot}} \approx \frac{T}{\sigma\Theta_{\mathrm{R}}}.$$

Θ_R also allows high and low temperatures. If $T >> \Theta_R$ say that T is a high temperature .If $T \approx \Theta_R$ or $T < \Theta_R$, then say T is a low temperature and we must use the summation formula (divided by the appropriate σ). For reasonable size molecules Θ_R is usually only a few degrees Kelvin. For light molecules it can be higher (for H_2, Θ_R = 87.57 K).

Nonlinear molecules have three moments of inertia and three rotational constants (and, hence, three Θ_R's). The three rotational constants A, B, and C, the rotational partition function (at high temperatures) is

$$q_{\mathrm{rot}} \approx \frac{\sqrt{\pi}}{\sigma} \frac{(kT)^{\frac{3}{2}}}{\sqrt{ABC}}.$$

σ is the symmetry number and it is the number of orientations of the molecule which are indistinguishable from each other (for benzene σ =12, for ammonia σ =3, etc).

Vibrational motion

Vibrational energies for one mode of vibration are

$$E_{\mathrm{v}} = h\nu(\mathrm{v} + \frac{1}{2}),$$

where v = 0, 1, 2, 3, . . . , and *ν*is the characteristic frequency of the oscillator. The vibrational partition function is

$$\begin{aligned} q_{\mathrm{vib}} &= \sum_{\mathrm{v}} e^{-\beta h\nu(\mathrm{v}+1/2)} \\ &= e^{-\beta h\nu/2} \sum_{\mathrm{v}} e^{-\beta h\nu \mathrm{v}}, \end{aligned}$$

which can be summed in closed form to give

$$q_{\mathrm{vib}} = e^{-\beta h\nu/2} \frac{1}{1 - e^{-\beta h\nu}}.$$

$$e^{-\beta h\nu\mathrm{v}} = \left(e^{-\beta h\nu}\right)^{\mathrm{v}}.$$)

Sometimes a characteristic vibrational temperature, Θ_{v}, is defined by

$$\Theta_{\mathrm{v}} = \frac{h\nu}{k},$$

and the partition function is written in terms of Θ_v instead of *hν/k*. Characteristic vibrational temperatures are usually several thousands of Kelvins except for very "soft" or low frequency vibrational modes.

(Or)

b) Derive an expression for vibrational partition function.

The vibrational energy levels of a diatomic are given by En = (n +1/2) hν (3.17) where is ν the vibrational frequency and n is the vibrational quantum number. In this case, it is easy to sum the geometric series shown below

n 0 1 - (n +) h / k T 2 i b q

e = ∞ ν ν = ∑ (3.18) - h / (2 k T) - h / k T - 2 h / k T B B B e (1 + e e +.....)

ν ν ν = + h /2 kT e − ν = (1 + x + x2 + x3 ....) (3.19)

h /2 k T e − ν = [1 / (1- x)] (3.20) where x h / k TB e − ν = which is less than 1. Threfore, h / 2 k T vib h / k T e q 1 e − ν − ν = − (3.21) vib h / k T 1 q 1 e− ν = − (3.22) if the zero of energy scale is at h /2kT ν . Analogous to Θr, a vibrational temperature Θv or Θvib may be defined as hcν /k, where, ν is the vibrational frequency in cm-1 .

26. a) What is Bose-Einstein distribution law? Derive the equation for it.

Bose-Einstein Statistics

For each case, deriving an expression for the number of microstates per macrostate, which represents the total number of ways an arbitrary particle distribution can arise when accounting for all possible energy levels. Let us first consider one energy level. The number of ways in which *Nj*bosons in a single energy level, *ε j* , may be distributed among *gj*energy states is equivalent to the number of ways in which *Nj*identical, indistinguishable objects may be arranged in *gj*different containers, with no limitation on the number of objects per container.

$$W_j = \frac{(N_j + g_j - 1)!}{N_j!\,(g_j - 1)!}$$

Because each energy level represents an independent event, the total number of ways of obtaining an arbitrary particle distribution becomes

$$W_{BE} = \prod_j W_j = \prod_j \frac{(N_j + g_j - 1)!}{N_j!\,(g_j - 1)!} \qquad (1)$$

In other words,*WBE*identifies the generic number of microstates per macrostate for Bose–Einstein statistics.

Taking the natural logarithm of Eq. (1), we obtain

$$\ln W_{BE} = \sum_j \{\ln(N_j + g_j)! \; - \; \ln N_j! \; - \ln g_j!\}$$

where we have neglected the unity terms since *gj*_ 1. Applying Stirling's approximation, i.e., ln*N*! = *N*ln*N*− *N* ,we find that

or

b) Explain the Einstein's theories of heat capacities of solids.

Einstein treated the atoms in a crystal as N simple harmonic oscillators, all having the same frequency ν_E. The frequency ν_E depends on the strength of the restoring force acting on the atom, i.e. the strength of the chemical bonds within the solid. Since the equation of motion for each atom decomposes into three independent equations for the x, y and z components of displacement, and N- atom solid is equivalent to 3N harmonic oscillators, each vibrating independently at frequency ν_E. Note that this treatment is a gross approximation, since in reality the lattice vibrations are very complicated coupled oscillations.

The energy levels of the harmonic oscillators are given by

$$\varepsilon_v = h\nu_E(v + \tfrac{1}{2}), \qquad v = 0, 1, 2\ldots$$