

LECTURE NOTES

Subject: Chemistry-III (Basic Physical-I)

Faculty: Dr. Monalisa Mohapatra

Subject Code: CH-211

3rd Semester 5 yr Int. M.Sc.

Module-I: (10 Hours)

Dilute Solutions: Vapour Pressure, Raoult's Law, and Thermodynamic Derivation of Laws Relating to Elevation of Boiling Point, Depression of Freezing Point and Osmotic Pressure. Ideal and Non-ideal Solution Association and Dissociation.

Module-II: (10 Hours)

Homogenous Equilibrium: Law of Mass Action and the Thermodynamic Derivation of the Expression for Equilibrium constant, Different forms of Equilibrium Constants. Le Chatelier's Principle, Illustrations with some Gaseous Reactions. Effect of Temperature on Equilibrium van't Hoff's Equation and its Integration.

Module-III: (10 Hours)

Chemical Kinetics: Order and Molecularity, Kinetics of Ist and IInd Order Reactions, Simple Opposing (A & B) Reaction, Consecutive or Sequential (A-B-C) Reaction, Chain Reaction (H_2+Br_2). Effect of Temperature on Reaction Rate. Collision Theory of Reaction Rate, Qualitative Treatment of Transition Theory.

Module-IV: (10 Hours)

Thermodynamic Concept: Heat Content and Heat Capacity Isothermal and Adiabatic Change, Work Done for Ideal and van der Waal Gases.

Thermochemistry: Heat Changes in Chemical Reactions, Hess's Law, Kirchoff's Equation.

2nd law of Thermodynamics: Spontaneous Process, Carnot's Theorem and Carnot's Cycle, Efficiency of Heat Engine, Entropy Changes in Reversible and Irreversible Processes, Free Energy and Work Function Condition for Equilibrium, Clapeyron and Clausius Equation, Gibb's Helmholtz Equation.

Prescribed Books:

1. P. Atkins and J. de Paula, *Elements of Physical Chemistry*, 6th Edition, Oxford University Press, 2013.
2. P. Atkins and J. de Paula, *Physical Chemistry*, 9th Edition, W. H. Freeman, 2009.
3. R.A. Alberty and R.J. Silbey, *Physical chemistry*, 2nd Edition, John Wiley & sons, 1997.
4. T. Engel and P. Reid, *Physical Chemistry*, 3rd Edition, Pearson Education, 2012.
5. K.J. Laidler, J.H. Meiser, and B.C. Sanctuary, *Physical Chemistry*, 4th Edition, Houghton Mifflin, 2003.

Referred Books:

1. G.N. Barrow, *Physical Chemistry*, 5th Edition, Tata McGraw-Hill, 2007.
2. K.L. Kapoor, *A Textbook of Physical Chemistry*, 2nd Edition, Macmillan, 2011.
3. H. Kuhn, H.-D. Försterling, and D.H. Waldeck, *Principles of Physical Chemistry*, 2nd Edition, John Wiley & sons, 2009.
4. R.G. Mortimer, *Physical Chemistry*, 3rd Edition, Elsevier, 2008.
5. I.N. Levine, *Physical Chemistry*, 6th Edition, McGraw-Hill, 2008.
6. G.W. Castellan, *Physical Chemistry*, 3rd Edition, Addison Wesley, 1983.

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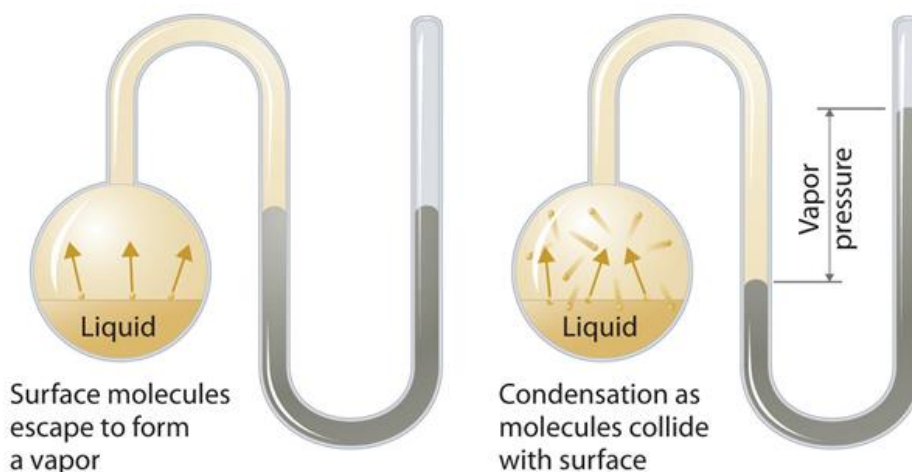
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MODULE-I

VAPOUR PRESSURE:

Consider a pure liquid in a beaker is covered with a jar. Some molecules on the liquid surface evaporate and fill the vacant space available to them. The molecules in the vapour phase move randomly in the vacant space, during this motion, they strike the surface of the liquid and condensed. This process of evaporation and condensation go on and an equilibrium is established between evaporation and condensation. The pressure exerted by vapours over the liquid surface at equilibrium is called *vapour pressure* of the liquid.

If solute is non-volatile solid or liquid the vapour pressure of solution is equal to partial vapour pressure of solvent in the solution and if the solute is volatile solid or liquid, then vapour pressure will be equal to the sum of partial vapour pressure of solute and that of solvent.



RAOULT'S LAW:

In 1886, a French Chemist named Francois Marte Raoult proposed a quantitative relation between partial pressure and mole fraction of volatile liquids. The law states that mole fraction of the solute component is directly proportional to its partial pressure.

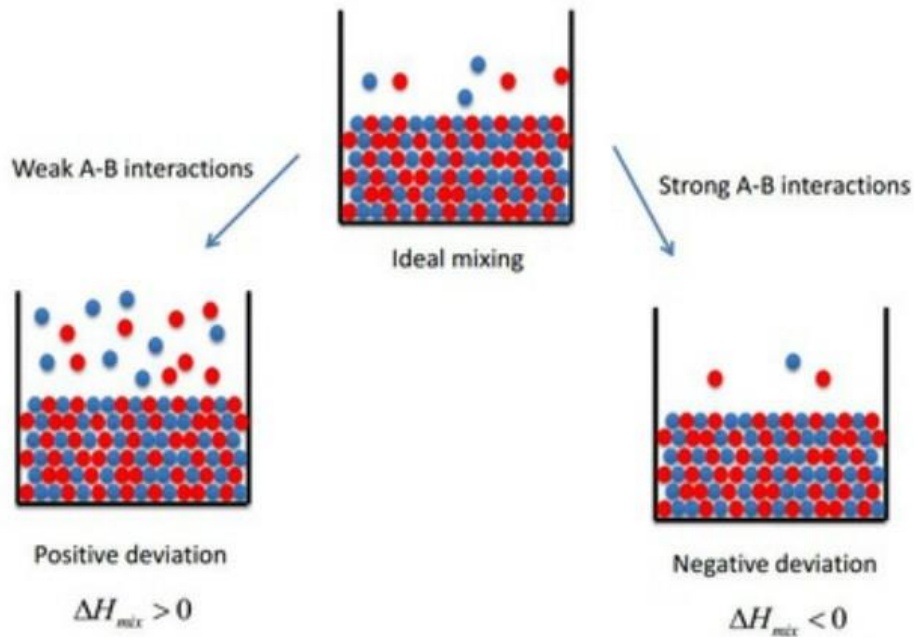


Image 1: Types of Solutions

On the basis of Raoult's Law, liquid-liquid solutions are classified into two types of solutions, they are:

- Ideal Solutions
- Non-ideal Solutions

Ideal and Non – Ideal Solutions

The solutions which obey Raoult's law at all compositions of solute in solvent at all temperature are called **ideal solutions**.

Ideal solutions can be obtained by mixing two components with identical molecular size, structure and they should have almost same inter molecular attraction e.g., two liquids A and B form an ideal solution when A –A and B–B molecular attractions will be same and hence A–B molecular attraction will be almost same as A–A and B–B molecular attraction.

An ideal solution should have following characteristics

- It should obey Raoult's law i.e., $P_A = X_A$ and $P_B = X_B$
- $\Delta H_{mixing} = 0$, i.e. no heat should be absorbed or evolved during mixing

- $\Delta V_{\text{mixing}} = 0$, i.e. no expansion or contraction on mixing ?

Examples of Ideal solutions

- Ethyl chloride and ethyl bromide
- n-hexane and n-heptane
- CCl_4 and SiCl_4

The solution which deviate from ideal behaviour are called **non ideal solution** or **real solutions** and they do not obey Raoult's law over entire range of composition.

It has been found that on increasing dilution, a non ideal solution tend to be ideal.

For non ideal solutions,

- $P_A \neq X_A P_A^0$, $P_B \neq X_B P_B^0$ i.e, they do not obey Raoult's law
- $\Delta H_{\text{mixing}} \neq 0$,
- $\Delta V_{\text{mixing}} = 0$

Here we may have two cases

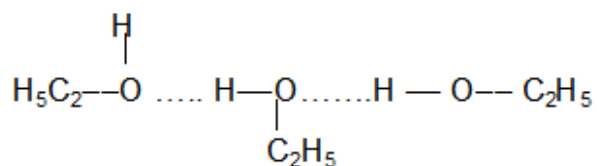
Case 1:

- $P_A > X_A P_A^0$ & $P_B > X_B P_B^0$
- $\Delta H_{\text{mix}} > 0$
- $\Delta V_{\text{mix}} > 0$

Such a solution shows **positive deviation** from Raoult's Law and the observed boiling point of such solutions is found to be less than the calculated value. e.g. cyclohexane and ethanol.

In ethanol the molecules are held together due to hydrogen bonding, when cyclohexane is added to ethanol the molecules of cyclohexane tend to occupy the space between ethanol molecules due to which some hydrogen bonds break due to which inter molecular attraction

between cyclohexane and ethanol is reduced and hence show higher vapour pressure.



Examples of solutions showing positive deviation:

- Acetone + Ethanol
- Acetone- Benzene
- Water + Methanol
- Water + Ethanol

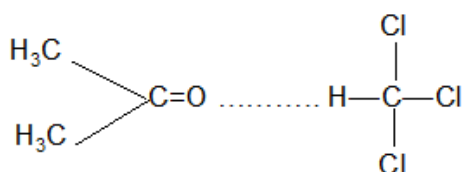
Case 2:

$$P_A < X_A P_A^0, \quad P_B < X_B P_B^0$$

$$\Delta H_{\text{mix}} < 0$$

$$\Delta V_{\text{mix}} < 0$$

Solutions of above type show *negative deviation* from Raoult's law and their observed boiling point is found to be higher than the calculated value eg. When acetone and chloroform are mixed together a hydrogen bond is formed between them which increases inter molecular attraction between them and hence decreases the vapour pressure



Examples of solutions showing negative deviation:

- Acetone + Aniline
- Chloroform + Diethyl ether
- Chloroform + Benzene
- Water + HCl

Condition for forming non-ideal solution showing positive deviation

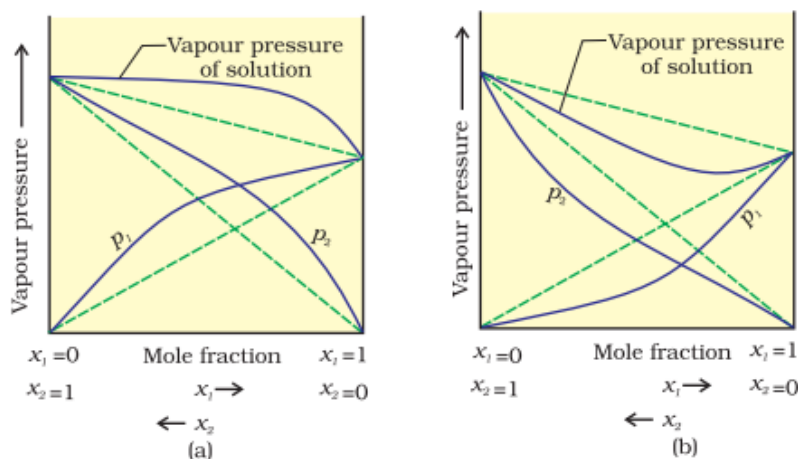
Two liquids A & B on mixing form this type of solutions when

- A-B attractive force should be weaker than A-A and B-B attractive force.
- “A” and “B” have different shape, size and character.
- “A” and “B” escape easily showing higher vapour pressure than the expected value.

Condition for forming non-ideal solution showing negative deviation

Two liquids A & B on mixing form this type of solutions when

- A-B attractive force should be greater than A-A and B-B attractive force.
- “A” and “B” have different shape, size and character.
- Escaping tendency of both “A” and “B” is lower showing lower vapour pressure than expected ideally.



Comparison between Ideal and Non-ideal solution

Ideal solutions	Non-ideal solutions	
	Positive deviation from Raoult's law	Negative deviation from Raoult's law
Obey Raoult's law at every range of concentration.	Do not obey Raoult's law.	Do not obey Raoult's law
$\delta H_{\text{mix}} = 0$; neither is evolved nor absorbed during dissolution.	$\delta H_{\text{mix}} > 0$. Endothermic dissolution; heat is absorbed.	$\delta H_{\text{mix}} < 0$. Exothermic dissolution; heat is evolved.

$\delta V_{\text{mix}} = 0$; total volume of solution is equal to sum of volumes of the components.	$\delta V_{\text{mix}} > 0$. Volume is increased after dissolution.	$\delta V_{\text{mix}} < 0$. Volume is decreased during dissolution.
$P = p_A + p_B = p_A^0 X_A + p_B^0 X_B$	$p_A > p_A^0 X_A$; $p_B > p_B^0 X_B$ $\therefore p_A + p_B > p_A^0 X_A + p_B^0 X_B$	$p_A < p_A^0 X_A$; $p_B < p_B^0 X_B$ $\therefore p_A + p_B < p_A^0 X_A + p_B^0 X_B$
A—A, A—B, B—B interactions should be same, i.e., 'A' and 'B' are identical in shape, size and character.	A—B attractive force should be weaker than A—A and B—B attractive forces. 'A' and 'B' have different shape, size and character.	A—B attractive force should be greater than A—A and B—B attractive forces. 'A' and 'B' have different shape, size and character.
Escaping tendency of 'A' and 'B' should be same in pure liquids and in the solution.	'A' and 'B' escape easily showing higher vapour pressure than the expected value.	Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally.

AZEOTROPES:

Azeotropes are defined as a mixture of two liquids which has a constant composition in liquid and vapour phase at all temperatures. Azeotropes can't be separated by fractional distillation, as the composition of vapour phase remains same after boiling. Because of uniform composition azeotropes are also known as **Constant Boiling Mixtures**.

There are two types of Azeotropes:

- Maximum Boiling Azeotrope
- Minimum Boiling Azeotrope

Maximum Boiling Azeotrope

Maximum Boiling Azeotrope is formed when we mix two non-ideal solutions at some specific composition, showing large negative deviation from Raoult's law.

Examples:

- Nitric Acid (HNO_3) (68%) and water (32%) form maximum boiling azeotrope at boiling temperature of 393.5 K

- Hydrochloric Acid (HCl) (20.24%) and water form maximum boiling azeotrope at boiling temperature of 373 K

Minimum Boiling Azeotrope

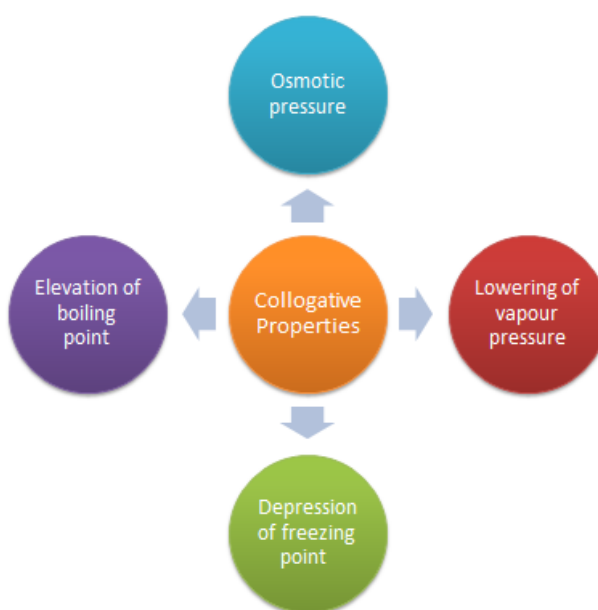
Minimum Boiling Azeotrope is formed when we mix two non-ideal solutions at some specific composition, which shows large positive deviation from Raoult's Law.

Example:

- Ethanol (95.5 %) and water (4.5 %) form minimum boiling azeotrope at boiling temperature of 351.5 K

COLLIGATIVE PROPERTIES:

A dilute solution is one in which the amount of the solute is very small in comparison to the amount of the solvent. The dilute solutions show more or less ideal behavior as the heat and volume changes, accompanying the mixing of solute and solvent, are negligible for all practical purposes. Dilute solutions obey Raoult's law. The properties of dilute solutions which depend only on number particles of solute present in the solution and not on their identity are called *colligative properties* (denoting depending upon collection).



We shall assume here that the solute is *non-volatile*, so it does not contribute to the vapour.

We shall also assume that the solute does not dissolve in solid solvent, that is, the pure solid solvent separates when the solution is frozen, the latter assumption is quite drastic, although it is true for many mixtures, it can be avoided.

Colligative properties are the properties of only dilute solution which are supposed to behave as ideal solutions. The various colligative properties are:

- Depression of freezing point
- Lowering of vapour pressure
- Osmotic pressure
- Elevation of boiling point

LOWERING OF VAPOUR PRESSURE BY NON VOLATILE SOLUTE:

It has been known for a long time that when a non-volatile solute is dissolved in a liquid, the vapour pressure of the solution becomes lower than the vapour pressure of the pure solvent.

In 1886, the French chemist, Francois Raoult, after a series of experiments on a number of solvents including water, benzene and ether, succeeded in establishing a relationship between the lowering of vapour pressure of a solution and the mole fraction of the non-volatile solute.

Let us consider a solution obtained by dissolving n moles of a non-volatile solute in N moles of a volatile solvent. Then mole fraction of the solvent, $X_1 = N/(n+N)$ and mole fraction of the solute, $X_2 = n/(N+n)$. Since the solute is non-volatile, it would have negligible vapour pressure. The vapour pressure of the solution is, therefore merely the vapour pressure of the solvent. According to Raoult's law, the vapour pressure of a solvent (P_1) in an ideal solution is given by the expression;

$$P_1 = X_1 P_1^0 \dots\dots\dots(1)$$

where P_1^0 is the vapour pressure of the pure solvent. Since $X_1 + X_2 = 1$, Eq. 1 may be written as

$$P_1 = (1 - X_2)P_1^0 \quad \dots (2)$$

$$\text{or } P_1/P_1^0 = 1 - X_2$$

$$\text{or } \frac{P_1^0 - P_1}{P_1^0} = X_2 \quad \dots (3)$$

The expression on the left hand side of Equation (3) is usually called the relative lowering of vapour pressure. Equation (3) may thus be stated as: '*The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute present in the solution.*'

This is one of the statements of the **Raoult's law**.

Since mole fraction of the solute, X_2 is given by $n/(N+n)$, Equation (3) may be expressed as

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{n}{N + n} \quad \dots (4)$$

It is evident from Equation (4) that the lowering of vapour pressure of a solution depends upon the number of moles (and hence on the number of molecules) of the solute and not upon the nature of the solute dissolved in a given amount of the solvent. Hence, *lowering of vapour pressure is a colligative property*.

Determination of Molar Masses from Lowering of Vapour Pressure

It is possible to calculate molar masses of non-volatile non-electrolytic solutes by measuring vapour pressures of their dilute solutions.

Suppose, a given mass, w gram, of a solute of molar mass m , dissolved in W gram of solvent of molar mass M , lowers the vapour pressure from P_1^0 to P_1 . Then, by Equation (4)

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{n}{N+n} = \frac{w/m}{W/M + w/m} \quad \dots(5)$$

Since in dilute solutions, n is very small as compared to N , Equation (5) may be put in the approximate form as

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{n}{N} = \frac{w/m}{W/M} = \frac{wM}{Wm} \quad \dots(6)$$

$$\text{or, } m = \frac{wM}{W (P_1^0 - P_1)/P_1^0}$$

Limitations of Raoult's Law

- Raoult's law is applicable only to very dilute solutions.
- It is applicable to solutions containing non-volatile solute only.
- It is not applicable to solutes which dissociate or associate in a particular solution.

Question

The density of a 0.438 M solution of potassium chromate at 298 K is 1.063 g cm^{-3} . Calculate the vapour pressure of water above this solution. Given : P^0 (water) = 23.79 mm Hg.

Solution

A solution of 0.438 M means 0.438 mol of K_2CrO_4 is present in 1L of the solution. Now,

Mass of K_2CrO_4 dissolved per litre of the solution = $0.438 \times 194 = 84.972 \text{ g}$

Mass of 1L of solution = $1000 \times 1.063 = 1063 \text{ g}$

Amount of water in 1L of solution = $978.028/18 = 54.255 \text{ mol}$

Assuming K_2CrO_4 to be completely dissociated in the solution, we will have;

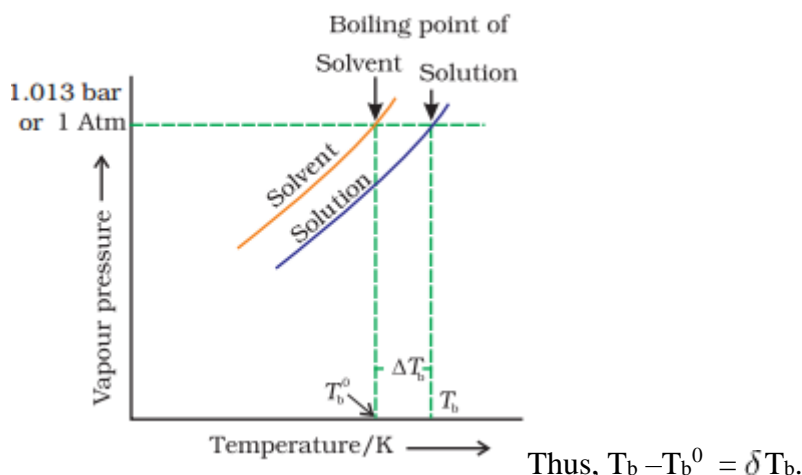
Amount of total solute species in the solution = $3 \times 0.438 = 1.314 \text{ mol}$.

Mole fraction of water solution = $54.335/(54.335+1.314) = 0.976$

Finally, Vapour pressure of water above solution = $0.976 \times 23.79 = 23.22$ mm Hg

BOILING POINT ELEVATION BY A NON-VOLATILE SOLUTE:

The boiling point of a liquid is the temperature at which its *vapour* pressure becomes equal to 760 mm (i.e. 1 atmospheric pressure). Since the addition of a non-volatile solute lowers the vapour pressure of the solvent, the vapour pressure of a solution is always lower than that of the pure solvent, and hence it must be heated to a higher temperature to make its vapour pressure equal to atmospheric pressure. Thus the solution boils at a higher temperature than the pure solvent. If T_b^0 is the boiling point of the solvent and T_b is the boiling point of the solution, the difference in boiling points (δT_b) is called the *elevation of boiling point*.



δT_b a molality where $\delta T_b =$ elevation of boiling point

$n =$ no. of moles of non-volatile solute

$N =$ Total no. of moles in the solution

This implies that the boiling point elevation in a dilute solution is directly proportional to the number of moles of the solute dissolved in a given amount of the solvent and is quite independent of the nature of the solute. Hence, *boiling point elevation is a colligative property*

$$\delta T_b = K_b \times m$$

k_b : molal elevation constant or Ebullioscopic constant

m : molality of the solution

Molal boiling point elevation constant or ebullioscopic constant of the solvent, is defined as the elevation in boiling point which may theoretically be produced by dissolving one mole of any solute in 1000 g of the solvent.

or

$$\Delta T_b = \frac{1000 \times K_b \times w}{m_1 \times W},$$

where m_1 = molecular weight of solute and w and W are weights of solute and solvent.

DEPRESSION OF FREEZING POINT BY A NON-VOLATILE SOLUTE:

Freezing point is the temperature at which solid and liquid states of a substance have the same vapour pressure. It is observed that the freezing point of the solution (T_f) containing non volatile solute is always less than the freezing point of the pure solvent (T_f^0). Thus, $T_f^0 - T_f = \delta T_f$

It can be seen that

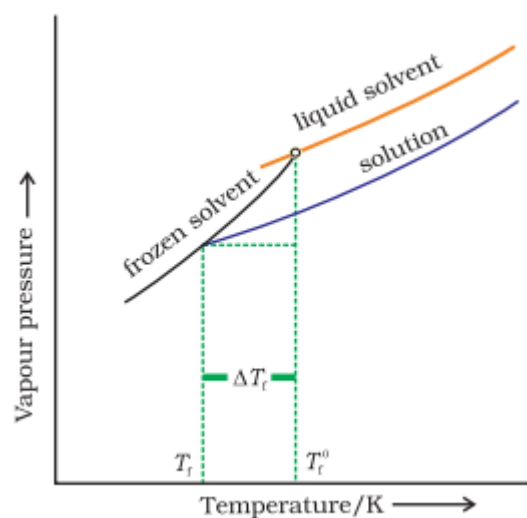
$$\delta T_f \propto \text{molality}$$

that, is freezing point depression of a dilute solution is directly proportional to the number of moles of the solute dissolved in a given amount of the solvent and is independent of the nature of solute

$$\text{or } \delta T_f = K_f m$$

k_f : molal freezing point depression constant of the solvent or cryoscopic constant

m : molality of the solution



Molal freezing point depression constant of the solvent or cryoscopic constant, is defined as the depression in freezing point which may theoretically be produced by dissolving 1 mole of any solute in 1000g of the solvent.

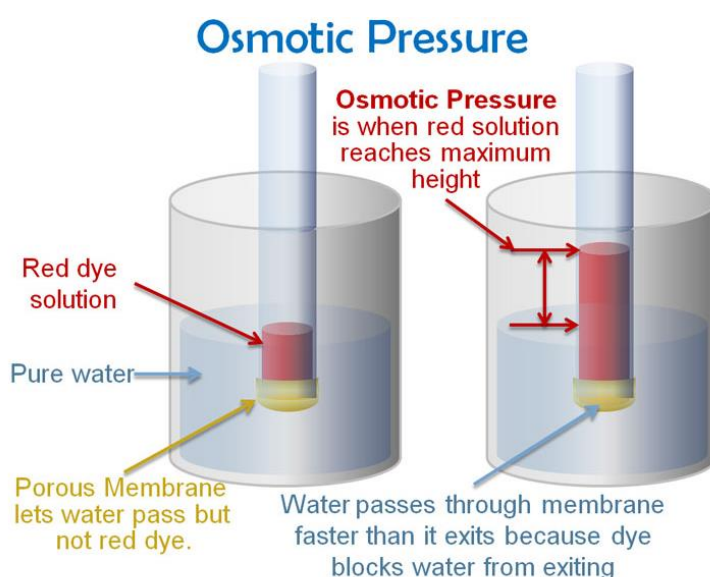
$$\Delta T_f = \frac{1000 \times K_f \times w}{m_1 \times W}$$

where m_1 = molecular weight of solute and w and W are weights of solute and solvent.

OSMOSIS AND OSMOTIC PRESSURE:

The phenomenon of the passage of pure solvent from a region of lower concentration (of the solution) to a region of its higher concentration through a semi-permeable membrane is called *osmosis*.

The driving force of osmosis is what is known as **osmotic pressure**. It is the difference in the pressure between the solution and the solvent system or it is the excess pressure which must be applied to a solution in order to prevent flow of solvent into the solution through the semi-permeable membrane. Once osmosis is complete the pressure exerted by the solution and the solvent on the semi-permeable membrane is same.



Van't Hoff equation for dilute solutions is (parallel to ideal gas equation)

$$\pi V = nRT$$

where π = Osmotic pressure

V= volume of solution

n= no. of moles of solute that is dissolved

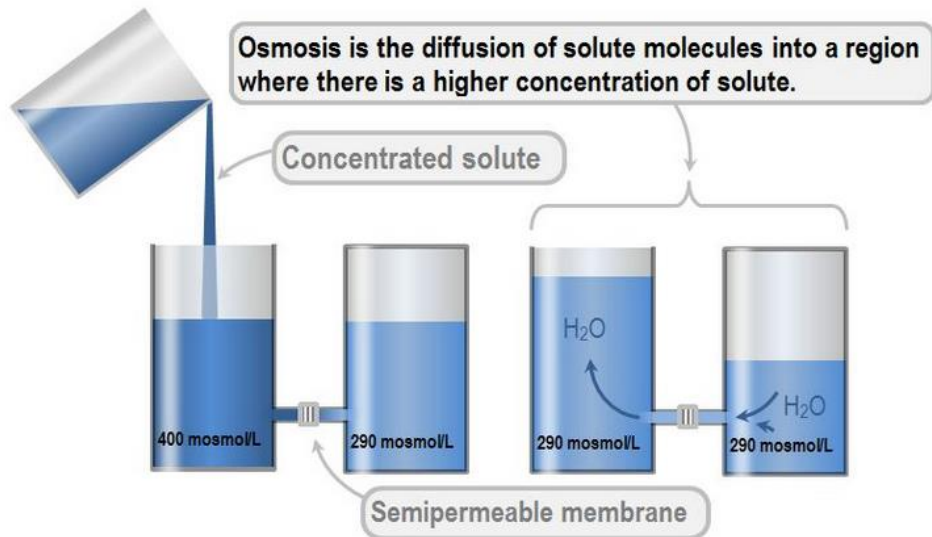
R = Gas constant

T= Absolute temperature

Isotonic Solutions: A pair of solutions having same osmotic pressure is called isotonic solutions.

Reverse Osmosis

When a solution is separated from pure water by a semipermeable membrane, water moves towards solution on account of osmosis. This process continues till osmotic pressure becomes equal to hydrostatic pressure or osmosis can be stopped by applying external pressure equal to osmotic pressure on solution. If external pressure greater than osmotic pressure is applied, the flow of solvent molecules can be made to proceed from solution towards pure solvent, i.e., in reverse direction of the ordinary osmosis. This type of osmosis is termed reverse osmosis. Reverse osmosis is used for the desalination of sea water for getting fresh drinking water.



Calculations with Colligative Properties

1. Vapor Pressure Lowering (Raoult's Law):

$$P_1 = X_1 P_1^\circ$$

P_1 = vapor pressure of the solution

X_1 = mol fraction of the solvent

P_1° = vapor pressure of the pure solvent

$$\Delta P = X_2 P_1^\circ$$

ΔP = the decrease in vapor pressure

X_2 = mol fraction of the solute

P_1° = vapor pressure of the pure solvent

2. Freezing Point Depression:

$$\Delta T_f = K_f m$$

ΔT_f = the decrease in freezing point

K_f = the freezing pt. depression constant ($^\circ\text{C}/m$)

m = molality of the soln (mol solute/kg solvent)

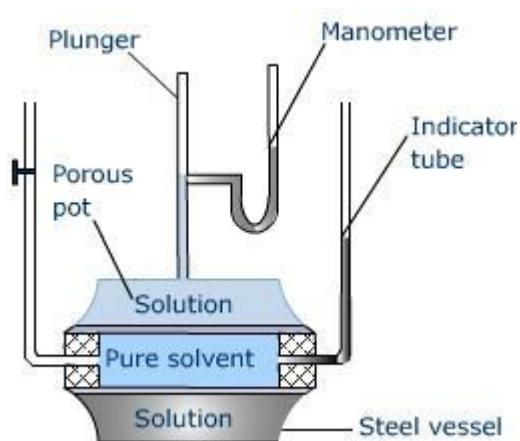
Determination of osmotic pressure: Berkeley and Hartley's method

Various methods are employed for the measurement of osmotic pressure but the best known method was suggested by Berkeley and Hartley. The apparatus used is shown in Fig. 5.11. A porcelain tube having copper ferrocyanide membrane in its walls is enclosed in a metallic jacket. The porcelain tube is fitted with a reservoir of pure solvent at one end and a capillary

tube at the other end. In a metallic jacket is an arrangement for applying external pressure which is measured with the help of pressure eggs.

Procedure:

The porcelain tube is filled with pure solvent and the metallic jacket with solution. The level in the capillary tube will tend to move down as the solvent flows towards solution due to osmosis. External pressure is now applied on the solution by the piston so that level in capillary remain stationary. The reading of pressure gauge is recorded. This is the osmotic pressure of the solution.



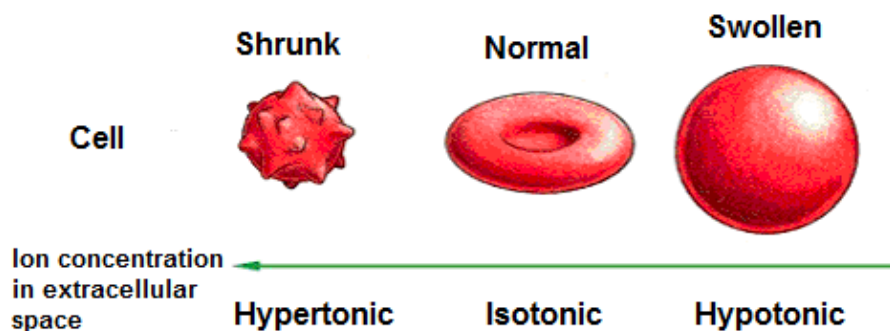
Advantages:

- It is a quick and accurate method.
- The concentration of the solution does not change because flow of solvent is not permitted into solution; so the results obtained by this method are reliable.
- As the osmotic pressure is balanced by external pressure, there is no strain on membrane and the danger of its bursting is eliminated. So, this method can be used to measure high osmotic pressure also.

Comparison of osmotic pressures:

de-Vries developed an approximate method for comparing the relative osmotic pressures of aqueous solutions. A solution of low osmotic pressure is termed hypotonic and solution of high osmotic pressure is termed hypertonic. The protoplasmic layer, lining the cell walls of plant cells is easily penetrated by water but is almost impermeable to the substances dissolved in the cellular fluid. When a plant cell is placed in a hypotonic solution, the water is drawn in and the cell swells. If the cell is placed in a hypertonic solution, water will diffuse out of the cell fluid and partial collapse of the cell will take place when a hypotonic solution is separated from a hypertonic solution using a semipermeable membrane then osmosis takes place from hypotonic to hypertonic because solvent concentration is greater in hypotonic solution. This phenomenon is known as plasmolysis.

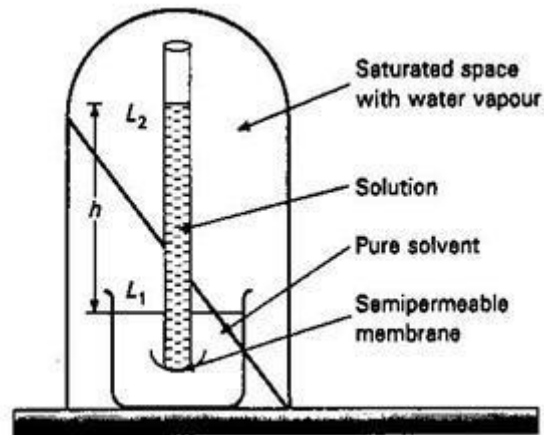
The change in cell can be placed in the solution of same osmotic pressure as that of the cell fluid, no change in the structure of the cell is observed. Such solutions having same osmotic pressures are termed isotonic. By putting, therefore, cells of the same kind into solutions of different concentrations, it can be ascertained whether the solution is hypertonic or hypotonic or isotonic.



Relation between osmotic pressure and vapour pressure

Let an aqueous dilute solution filled in a capillary tube is closed at one end by a semipermeable membrane. The tube is placed in pure solvent (water). Entire apparatus is closed by a belljar.

At osmotic equilibrium, the belljar is saturated with water vapour. At equilibrium osmotic pressure (π) becomes equal to hydrostatic pressure.



$$\pi = h \times d \quad \dots(i)$$

where 'h' is height in the column, π is osmotic pressure

Let p_0 = Vapour pressure of pure solvent

p = Vapour pressure of solution

Pressure at level $L_1 = p_0$; Pressure at level $L_2 = p$. Pressure at L_1 will be greater than pressure at L_2 . Then

$$P_0 - p = hD \quad \dots(ii)$$

where 'd' is density of solvent vapour of pressure p_0 .

Dividing Eq. (i) by (ii), we have,

$$\frac{\pi}{p_0 - p} = \frac{h \times d}{h \times D} = \frac{d}{D}$$

at a fixed temperature d/D is constant.

$$\therefore \pi = \text{constant} (p_0 - p) \quad \dots(iii)$$

$$\text{i.e., } \pi \propto (p_0 - p) \quad \text{or } \delta p \quad \dots(iv)$$

Thus, osmotic pressure is directly proportional to the lowering of vapour pressure.

We know that $p_0V = nRT$

$$p_0V = \frac{W}{M}RT$$

i.e.

$$p_0V = \frac{W}{V}RT = DRT$$

$$\therefore p_0 = \frac{RTD}{M} \dots\dots\dots(v)$$

Dividing Eq. (iii) by (v), we get

$$\frac{p_0 - p}{p_0} = \pi \frac{M}{dRT}$$

$$\frac{\Delta p}{p_0} = \pi \frac{M}{dRT}$$

At a fixed temperature, π and M/dRT are constant.

Thus, $\Delta p/p_0 \propto \pi$, i.e., Osmotic pressure is proportional to relative lowering of vapour pressure.

ABNORMAL COLLIGATIVE PROPERTIES AND VAN'T HOFF FACTOR:

Since colligative properties depend upon the number of particles of the solute, in some cases where the solute associates or dissociates in solution, abnormal results for molecular masses are obtained.

Van't Hoff Factor:

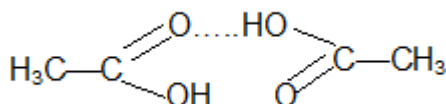
Van't Hoff, in order to account for all abnormal cases introduced a factor **i** known as the *Van't Hoff factor*, such that

$$i = \frac{\text{Observed colligative property (actual)}}{\text{Theoretical colligative property (expected)}}$$

$$= \frac{\text{No. of molecules actually present}}{\text{No. of molecules expected to be present}}$$

ASSOCIATION:

There are many organic solutes which in non-aqueous solutions undergo association, that is, two or more molecules of the solute associate to form a bigger molecule. Thus, the number of **effective** molecules decreases and, consequently the osmotic pressure, the elevation of boiling point or depression of freezing point, is less than that calculated on the basis of a single molecule. Two examples are : acetic acid in benzene and chloroacetic acid in naphthalene.

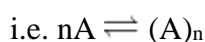


Association of Acetic acid in benzene through hydrogen bonding

Degree of Association:

The fraction of *the total number of molecules which combine to form bigger molecule.*

Consider one mole of solute dissolved in a given volume of solvent. Suppose n simple molecules combine to form an associated molecule,



Let a be the degree of association, then,

The number of unassociated moles = $1-a$

The number of associated moles = a/n

Total number of effective moles = $1-a+a/n$

$$i = \frac{1 - \alpha + \alpha/n}{1}$$

$$i = 1 - \alpha(1 - 1/n)$$

Obviously, $i < 1$

Question:

Acetic acid (CH_3COOH) associates in benzene to form double molecules. 1.65 g of acetic acid when dissolved in 100g of benzene raised the boiling point by 0.36°C . Calculate the Van't Hoff Factor and the degree of association of acetic acid in benzene (Molal elevation constant of benzene is 2.57).

Solution:

Normal molar mass of acetic acid = 60

Observed molar mass of acetic acid.

$$M = k_b \frac{w_{\text{solute}}}{w_{\text{solvent}} \Delta T} \times 1000$$

$$\frac{2.57 \times 1.65 \times 1000}{100 \times 0.36} = 118$$

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{60}{118} = 0.508$$

$$0.508 = 1 - \alpha(1 - 1/n) = 1 - (1 - 1/2\alpha) = 1 - 1/2\alpha$$

$$\alpha/2 = 1 - 0.508 = 0.492$$

$$\alpha = 2 \times 0.492 = \mathbf{0.984}$$

Thus acetic acid is **98.4%** associated in benzene.

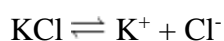
DISSOCIATION

Inorganic acids, bases and salts in aqueous solutions undergo dissociation, that is, the molecules break down into positively and negatively charged ions. In such cases, the number of *effective* particles increases and, therefore, osmotic pressure, elevation of boiling point and depression of freezing point are much higher than those calculated on the basis of an undissociated single molecule.

Degree of Dissociation

Degree of dissociation means *the fraction of the total number of molecules which dissociates in the solution, that is, breaks into simpler molecules or ions*. Consider one mole of a univalent electrolyte like potassium chloride dissolved in a given volume of water. Let α be its degree of dissociation.

Then the number of moles of KCl left undissociated will be $1-\alpha$. At the same time, α moles of K^+ ions and α moles of Cl^- ions will be produced, as shown below.



Thus, the total number of moles after dissociation = $1-\alpha+\alpha+\alpha = 1+\alpha$

Hence, $i = (1+\alpha)/1$

Since, as already, mentioned, osmotic pressure, vapour pressure lowering, boiling point elevation or freezing point depressions vary inversely as the molecular weight of the solute, it follows that

$$i = 1 + \alpha = 1 + (2-1)\alpha$$

In general, $i = 1 + (n-1) \alpha$, Where, n = number of particles (ions) formed after dissociation

From the above formula, it is clear that $i > 1$

Knowing, the observed molar mass and the Van't Hoff factor, i , the degree of dissociation, α can be easily calculated.

Now, if we include Van't Hoff factor in the formulae for colligative properties we obtain the normal results.

$$\text{Relative lowering of vapour pressure, } \frac{P_1^\circ - P_1}{P_1^\circ} = iX_2 = i \frac{n}{n+N}$$

$$\text{Osmotic pressure, } \pi = iCRT$$

$$\text{Elevation in boiling point, } \Delta T_b = i \cdot 1000 \times K_b \times \text{molality}$$

$$\text{Depression in freezing point, } \Delta T_f = i \cdot 1000 \times K_f \times \text{molality}$$

Note: The value of i is taken as **one** when solute is non electrolyte.

MODULE -II

INTRODUCTION TO CHEMICAL EQUILIBRIUM:

In discussing stoichiometry, we often assume that all reactions go to completion and that the amount of product(s) obtained depends on the amount and stoichiometric relationship of the limiting reactant to product(s). Some reactions go to completion. The following class reactions are examples of these types of reactions:

1. Acid-base reactions;
2. Precipitation reactions;
3. Oxidation-reduction reactions (electron transfer reactions).
4. Reactions in which nonelectrolytes are formed.

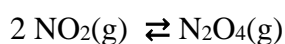
However, many reactions, especially those involving gases, generally do not go to completion. In fact, reverse reactions occur before the limiting reactants get completely used up. All gaseous reactions in a closed system undergo reversible processes and the following are some examples:

1. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$;
2. $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$;
3. $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$;

In aqueous solutions, the dissociations of weak acids and bases and the dissolution of slightly soluble salts are reversible processes.

1. $\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$;
2. $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$;
3. $\text{Mg}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$;

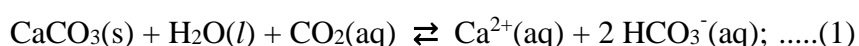
Consider the following reaction that occurs in a closed container:



If an amount of NO₂ gas is placed in a sealed container and let it stands at room temperature, the brownish color of the gas slowly fades (or becomes less intense). This is because the forward reaction that changes some of NO₂ (brown) to N₂O₄ (colorless) has taken place. The fading of the color may continue for some times as more and more of NO₂ gas is converted to N₂O₄, but this change apparently seems to stop at some point when the reaction has reached a state of *equilibrium*. Equilibrium occurs because the reversible or processes occur at the same rate.

All chemical reactions carried out in a closed system are essentially reversible and will eventually reach a state of equilibrium, at which concentrations of components in the reaction mixture remain unchanged even when the mixture is left for a longer period at constant temperature.

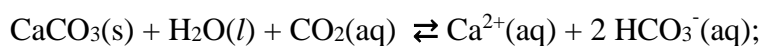
Many chemical processes in nature also occur in reversible manner and established equilibrium. For example, the formation of stalactite and stalagmite in limestone caves are the results of reversible reactions. When rain water saturated with dissolved CO₂ seeps through limestone hills (composed mainly of CaCO₃), the following reaction occurs in which some of CaCO₃ (limestone) are dissolved.



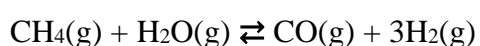
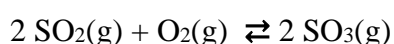
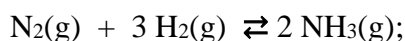
The rain water that sieve through the rocks becomes saturated with Ca²⁺ and HCO₃⁻ ions causing the reverse reaction to occur, depositing CaCO₃ that eventually form the *stalactites* and *stalagmites*.



We may say that the formation of stalactite and stalagmite in limestone caves is the result of the following reversible reactions:

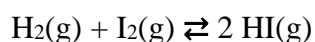


Some reactions occur at a significantly fast rate and reach equilibrium within minutes. Precipitation and acid-base reactions are examples of reactions that quickly reach equilibrium. Other reactions occur very slowly and may take weeks if not months or years to reach equilibrium. The following reactions are examples of these slow reactions. They are usually carried out at high temperature and in the presence of catalysts:



THE EQUILIBRIUM CONDITIONS

All chemical reactions are preceded by molecular collisions, but only those collisions with proper orientation and sufficient energy to form the transition state complex would subsequently lead to the formation of products. Consider the following reversible reaction:

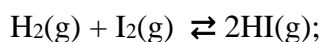


which consists of forward and reverse processes:

Forward reaction: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2 \text{HI}(\text{g}) \dots(1)$; Reverse reaction: $2 \text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g}) \dots(2)$

1. The rate of forward reaction (equation-1) depends on the frequency of collisions, which in turn depends on the concentrations of H_2 and I_2 .
2. As HI molecules are formed, they also collide with each other and some of them dissociate to form H_2 and I_2 according to equation-2 - the reverse process.
3. As both opposing reactions progress, the concentration of products increases and so the rate of the reverse reaction. At the same time, the reactant concentrations and the rate of forward reaction decrease.
4. Eventually, the rates of the two opposing processes become equal and there is no net change in the concentrations of the reacting species.

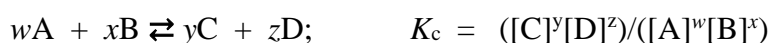
5. A state of dynamic chemical equilibrium is established, such as,



Equilibrium is *the exact balancing of two opposing processes*. It is a dynamic state, where both forward and reverse processes continue with equal rates. At equilibrium, the concentrations of all species in the system remain constant.

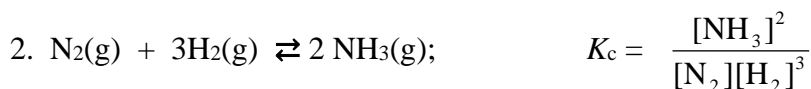
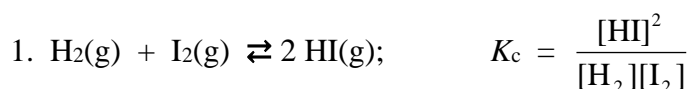
LAW OF MASS ACTION:

Consider a reaction involving a homogeneous system, such that their equilibrium is represented by the *law of mass action*:



where, A, B, C, and D are chemical species, and w , x , y , and z are their respective coefficients.

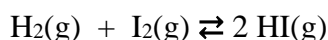
The equilibrium constant, K_c , for similar systems, as shown in the examples below, can be expressed as follows:



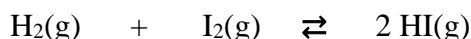
[Note: All concentrations for calculating K_c are those measured at equilibrium.]

Determining The Equilibrium Constant, K_c

Suppose that 0.1000 mole each of H_2 and I_2 are placed in 1.000-L flask, stoppered, and the mixture is heated to 425°C . At equilibrium, the concentration of I_2 is found to be 0.0210 M. What are the equilibrium concentrations of H_2 and HI , respectively? Calculate K_c for the following reaction at 425°C .



Calculate the concentration of H_2 , I_2 and HI at equilibrium using the ICE table:

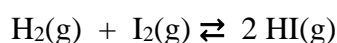


Initial [], M:	0.1000	0.1000	0.0000
Change in [], M:	-0.0790	-0.0790	+(2 x 0.0790)
Equilibrium [], M	0.0210	0.0210	0.1580

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.1580)^2}{(0.0210)^2} = 56.6$$

For a given reaction at constant temperature, the value of K_c does not depend on the amounts of reactants that are initially mixed, nor on any specific set of concentrations at equilibrium. For a given reaction, different sets of concentrations may occur at equilibrium, but the same value of K_c will be obtained at a given temperature. K_c depends on how the chemical equation is written, but not on how the reaction is carried out.

For example, supposed that 0.05000 mole of HI is placed in a 1.000-L flask, and the mixture is sealed and heated to 425°C. At equilibrium, the concentration of I_2 is found to be 0.00525 M. Calculate $[\text{H}_2]$ and $[\text{HI}]$ at equilibrium, and the value of K_c for the reaction:



Calculate the concentration of H_2 , I_2 and HI at equilibrium using the **ICE** table:

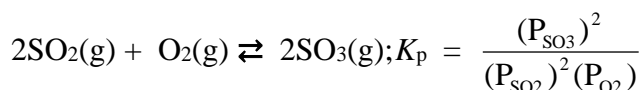
	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2 \text{HI}(\text{g})$
Initial [], M:	0.00000		0.00000		0.05000
Change in [], M:	+0.00525		+0.00525		-(2 x 0.00525)
Equilibrium [], M	0.00525		0.00525		0.03950

$$K_c = \frac{(0.0395)^2}{(0.00525)^2} = 56.6$$

The initial reaction may occur in the reverse direction and the equilibrium mixture may contain a different set of concentrations, but the value of K_c for the reaction at any given temperature will remain constant. Each set of equilibrium concentrations is called **equilibrium position**. Thus, *a given reaction at a fixed temperature has only one K_c value*, but it can have a finite number of *equilibrium positions*.

EQUILIBRIUM EXPRESSIONS INVOLVING PARTIAL PRESSURES

For reactions involving gaseous species, the equilibrium constant may be expressed in terms of partial pressures and denoted as K_p . For example,



Relationship between K_p and K_c :

Consider the equilibrium: $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$;

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}; \quad K_p = \frac{(P_{\text{SO}_3})^2}{(P_{\text{SO}_2})^2(P_{\text{O}_2})};$$

Assuming ideal gas behavior: $PV = nRT$, we derive the following relationships:

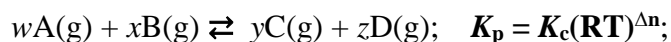
$$P_{\text{SO}_3} = (n_{\text{SO}_3})RT/V; \quad P_{\text{SO}_2} = (n_{\text{SO}_2})RT/V; \quad P_{\text{O}_2} = (n_{\text{O}_2})RT/V$$

$$(n_{\text{SO}_3})/V = (P_{\text{SO}_3})/RT = [\text{SO}_3]; \quad (P_{\text{SO}_2})/RT = [\text{SO}_2]; \quad (P_{\text{O}_2})/RT = [\text{O}_2]$$

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(P_{\text{SO}_3}/RT)^2}{(P_{\text{SO}_2}/RT)^2(P_{\text{O}_2}/RT)} = \frac{(P_{\text{SO}_3})^2}{(P_{\text{SO}_2})^2(P_{\text{O}_2})} \times (RT) = K_p(RT)$$

For the reaction: $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$, $K_c = K_p(RT)$, or $K_p = K_c(RT)^{-1}$

In general, for reactions involving gases, such as:

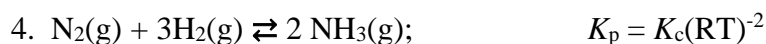


where $\Delta n = (y + z) - (w + x)$; (w , x , y , and z are coefficients of gas species only)

Other examples: 1. $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}); \quad K_p = K_c(\text{RT});$

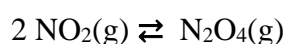
2. $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g}); \quad K_p = K_c(\text{RT})^{-1}$

3. $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g}); \quad K_p = K_c;$

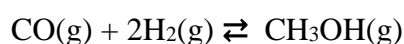


Exercise-1:

1. 0.160 mol NO₂ and 0.0400 mol N₂O₄ are placed in a 10.0-L sealed container. When equilibrium is reached at 353 K, the equilibrium concentrations were: [NO₂] = 0.0210 M. What is the molar concentration of N₂O₄ at equilibrium? Calculate the value of K_c and K_p, respectively, at 353 K for the reaction:



2. Methanol (or methyl alcohol) is produced commercially according to the following reaction:

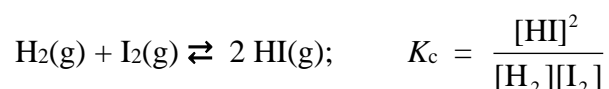


Suppose that in an experiment, 1.000 mol each of CO and H₂ are allowed to react in a sealed 10.0-L vessel. When equilibrium is established at 500 K, the concentration of CH₃OH was 0.00892 M. What are the equilibrium concentrations of CO and H₂? Calculate the equilibrium constants K_c and K_p, respectively, for the reaction at 500 K? (R = 0.0821 L.atm/Mol.K)

RELATIONSHIP BETWEEN EQUILIBRIUM EQUATIONS AND EQUILIBRIUM CONSTANTS:

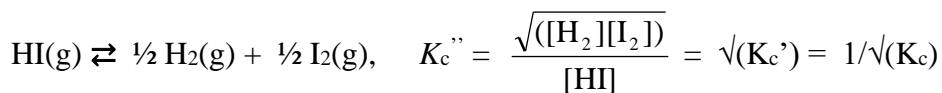
The equilibrium constant is expressed depending on how the equilibrium equation is written.

For example, for the following equilibrium:



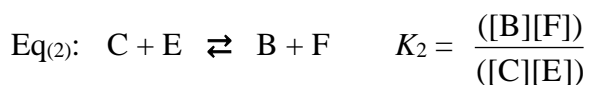
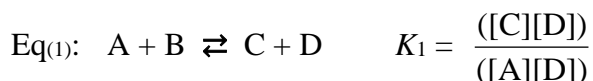
For the reverse reaction: $2 \text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g}); \quad K_c' = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = 1/K_c;$

If the reverse equation is divided by 2 and written as:



In fact, when two or more equations are added to yield a net equation, the equilibrium constant for the net equation, K_{net} , is equal to the product of equilibrium constants, K_i , of individual equations.

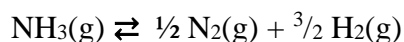
For example,



where, $\text{Eq(3)} = \text{Eq(1)} + \text{Eq(2)}$; and $K_3 = K_1 \times K_2$

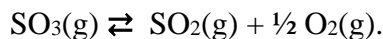
Exercise-2:

- The equilibrium constant for the reaction: $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$,
is $K_c = 3.6 \times 10^8$ at 298 K. What is the equilibrium constant for the following reaction,



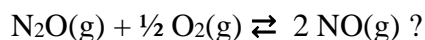
- For the reaction: $2 \text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2 \text{SO}_3\text{(g)}$, $K_c = 280$ at 1000 K.

What is the equilibrium constant for the following decomposition of SO_3 at 1000 K?



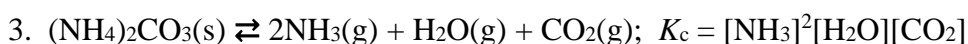
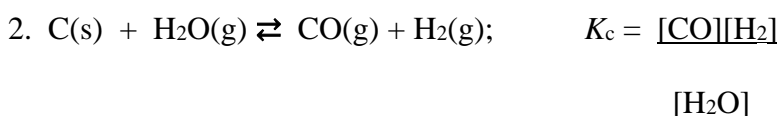
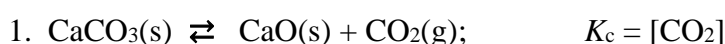
- Given: (1) $\text{N}_2\text{(g)} + \frac{1}{2} \text{O}_2\text{(g)} \rightleftharpoons \text{N}_2\text{O(g)}$; $K_{c(1)} = 2.4 \times 10^{-18}$
(2) $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2 \text{NO(g)}$; $K_{c(2)} = 4.1 \times 10^{-31}$

What is the equilibrium constant for the reaction:

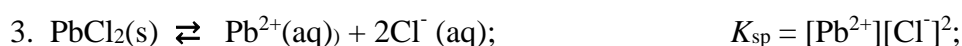
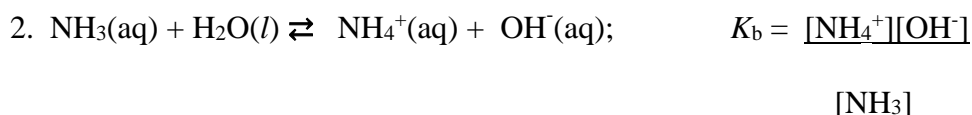
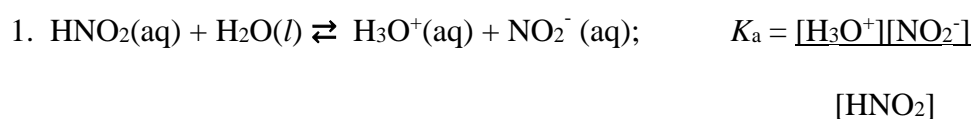


HETEROGENEOUS EQUILIBRIA:

In systems that involve components of different phases, such as solids and gases, liquids and gases, or solution and pure liquid, the concentration terms for the pure substances (solid or liquids) are not included in the expression of K_c . This is because the concentrations of such substances are constant, regardless of the quantity. For example, the concentration of pure water is about $56 M$, regardless of its volume. Examples of equilibrium constant expressions in heterogeneous equilibria are:



The following are examples of equilibria in aqueous solution:



(K_a , K_b , and K_{sp} are respectively called acid ionization, base ionization, and solubility product constants.)

APPLICATIONS OF THE EQUILIBRIUM CONSTANT:

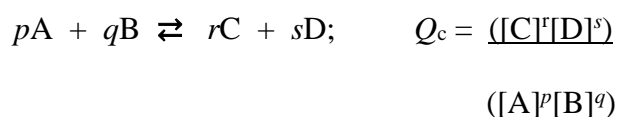
Knowing the equilibrium constant for a reaction allows us to predict:

- The extent of the reaction when equilibrium is established, but not the rate of reaction;
- Whether a given set of concentrations represents an equilibrium condition;
- The direction of net reaction from a given set of initial concentrations.

The value of the equilibrium constant for a reaction enable us to say whether the reaction under a given conditions favors product formation or tends to remain mainly on the reactant side. However, equilibrium constant does not tell us how fast equilibrium will be achieved.

USING EQUILIBRIUM CONSTANT TO PREDICT THE DIRECTION OF NET REACTION:

For a reaction of known K_c value, the direction of net reaction can be predicted by calculating the reaction quotient, Q_c . Reaction quotient is expressed in the same manner as K_c , except that the concentrations used are not necessarily the equilibrium concentrations. Consider the reaction:



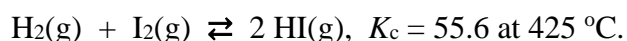
If $Q_c = K_c$, \rightarrow the reaction has reach equilibrium;

If $Q_c < K_c$, \rightarrow the reaction is not at equilibrium and there's a net forward reaction;

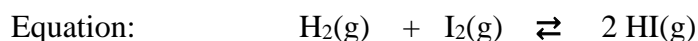
If $Q_c > K_c$, \rightarrow the reaction is not at equilibrium and there's a net reaction in reverse direction.

Calculating Equilibrium Concentrations from Initial Concentrations and K_c

If the equilibrium constant K_c for a reaction and the initial concentration(s) of reactants are known, the concentration of each component at equilibrium can be calculated. For example, consider the reaction:



If the initial concentrations of H_2 and I_2 are 1.000 M each, and the initial concentration of HI is 0.000, then the concentrations of components in the equilibrium mixture at 425 $^\circ\text{C}$ can be calculated as follows:



Initial [], M	1.000	1.000	0.000
Change [], M	-x	-x	+2x
Equilibrium [], M	(1.000 - x)	(1.000 - x)	2x

$$K_c = \frac{[\text{HI}]^2}{([\text{H}_2][\text{I}_2])} = \frac{(2x)^2}{(1.000 - x)^2} = 55.6$$

$$\frac{2x}{(1.000 - x)} = \sqrt{55.6} = 7.46$$

$$2x = 7.46 - 7.46x; \quad \rightarrow 9.46x = 7.46, \text{ and } x = 0.789;$$

At equilibrium, $[\text{H}_2] = 0.211 \text{ M}$; $[\text{I}_2] = 0.211 \text{ M}$, and $[\text{HI}] = 1.58 \text{ M}$

Exercise-3:

1. The reaction: $\text{CO}(\text{g}) + 2 \text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$, has $K_c = 14.5$ at 500 K.

Determine whether the following mixture containing 1.25 mol of H_2 , 1.00 mol of CO , and 0.050 mol of CH_3OH in a 10.0-L vessel at 500 K is at equilibrium. If not, predict the direction of net reaction that will take place to reach equilibrium.

2. For the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$, $K_p = 0.147$ at 353 K.

If the initial pressure of NO_2 is 0.921 atm, and initially there was no N_2O_4 , what is the total pressure of gases at equilibrium at 353 K?

3. The reaction: $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ has $K_c = 0.0896$ at a certain temperature. If 0.0860 mol of PCl_5 is placed in an empty 1.00-L flask, what would be the concentrations of PCl_5 , PCl_3 , and Cl_2 at equilibrium?

THERMODYNAMIC DESCRIPTION OF THE EQUILIBRIUM STATE:

Ideal gas at constant T, change pressure:

$$\Delta G = \Delta H - T\Delta S = -T\Delta S, \text{ since } \Delta H = 0$$

$$\text{but } \Delta S = \frac{q_{\text{rev}}}{T} \quad \text{and } q_{\text{rev}} = nRT \ln \left(\frac{V_2}{V_1} \right), \quad (\text{ch 7.6})$$

$$\therefore \Delta S = nR \ln \left(\frac{V_2}{V_1} \right), \quad (\text{ch 8.5})$$

$$= nR \ln \left(\frac{P_1}{P_2} \right) = -nR \ln \left(\frac{P_2}{P_1} \right)$$

$$\Delta G = nRT \ln \left(\frac{P_2}{P_1} \right) = nRT \ln \left(\frac{P}{P_{\text{ref}}} \right)$$

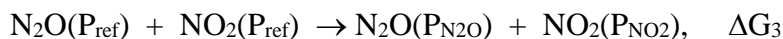
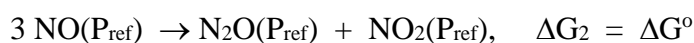
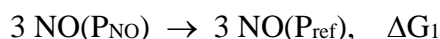
if choose $P_1 = 1 \text{ atm}$, the reference state, (then ignore $P_1 = P_{\text{ref}}$ only if in units of atm)

Gas-phase reactions



If all at 1 atm, 25°C, then $\Delta G = \Delta G^\circ$

If not, then treat as 3-step process:



$$\text{Overall: } \Delta G = \Delta G_1 + \Delta G^\circ + \Delta G_3$$

$$= \Delta G^\circ + RT \ln \left\{ \frac{(P_{\text{N}_2\text{O}})(P_{\text{NO}_2})}{(P_{\text{NO}})^3} \right\}$$

but at equilibrium, $\Delta G = 0$, hence $\Delta G^\circ = -RT \ln K_p$ (constant T)

note: K is dimensionless when P's in atm and P_{ref} 's = 1 atm

In general:



$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

Reactions in Ideal Solution

$$\Delta G^\circ = -RT \ln \left(\frac{[C]^c [D]^d}{[A]^a [B]^b} \right) = -RT \ln K_c$$

LE CHATELIER'S PRINCIPLE AND THE SHIFT IN EQUILIBRIUM POSITION:

Le Chatelier's principle states that *when factors that influence an equilibrium are changed, the equilibrium will shift to a new position that tends to minimize those changes.*

Understanding the factors that control the equilibrium positions of a chemical reaction is very important in chemical manufacturing. Chemists and chemical engineers in charge of production want to choose conditions that would give an optimum yield of the desired products. They would want the equilibrium to lie as far to the product side as possible. Three important factors that influence equilibrium are:

- Concentration, pressure, and temperature

1. The Effect of Concentration Change

Consider the reaction: $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g}); \quad K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$

Increasing the concentration of either N_2 or H_2 (or both) after an equilibrium has been established, will make $Q_c < K_c$, and a net forward (left to right) reaction occurs. Similar result is obtained if some of NH_3 is removed from the mixture. On the other hand, if some of N_2 or H_2 is removed or NH_3 is added to the equilibrium mixture, it will make $Q_c > K_c$, and a net reaction in the opposite direction will occur until a new equilibrium position is established.

By periodically adding new batches of N_2 and H_2 gases to the reactor and removing the product (NH_3), the above reaction will continuously proceed in the forward direction.

2. The Effect of Changing Pressure by changing Volume

(a) For a reaction such as: $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$,

the forward reaction would result in a decrease in pressure due to less number of gaseous molecules. While the reverse reaction increases the number of molecules and result in an increase in the total pressure. If the reaction mixture is forced into a smaller volume, the pressure will increase. According to Le Chatelier's principle, the system will proceed in the

forward reaction to reduce the pressure. For this type of reactions, the forward reaction favors a high pressure condition. If the reaction mixture is transferred to a larger container, the total gas pressure will drop and a net reaction will proceed in the reverse direction to reach new equilibrium position.

(b) For a reaction such as: $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$,

the products contain more gaseous molecules. The equilibrium will shift towards the reactants side if pressure is increased by compression of the reaction mixture. This type of reactions favors low pressure conditions.

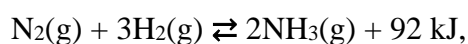
(c) Reactions such as: $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$ or $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$,

Has equal number of gaseous molecules on both sides. Changing the overall pressure will not affect the state of equilibrium. Any changes in pressure imposed on the system have equal effects on both sides.

(d) Note that a pressure change that is not due to volume change has no effect on the equilibrium of a reaction. Equilibrium is not influenced by a pressure change that is due to addition of gases not involved in the equilibrium system. For example, introducing helium gas into an equilibrium mixture containing H_2 , N_2 , and NH_3 , will not affect its equilibrium?

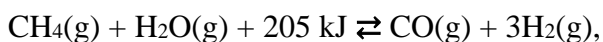
3. The Effect of Changing Temperature on Equilibrium

To realize the effect of temperature on equilibrium, we have to know whether a reaction is exothermic or endothermic. For example, the reaction:



is an exothermic reaction – heat is a product. Increasing the temperature means that heat is added to the system, and the system responds by going in the opposite direction (forming the reactants), which is the direction that absorbs heat. If the temperature is lowered (heat is removed), a net forward reaction will occur to produce more heat. Thus, *exothermic reactions favor a low temperature condition.*

The following is an endothermic reaction:

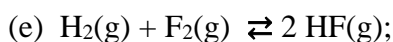
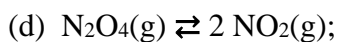
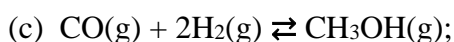
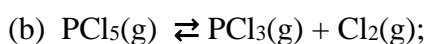
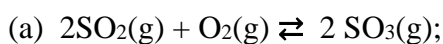


Increasing the temperature causes the reaction to go forward (in direction that removes heat from the system) to reduce the stress. This type of reactions favors a high temperature condition. Thus, *endothermic reactions favor a high temperature condition, and exothermic reactions favors low temperatures.*

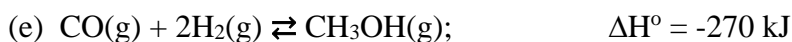
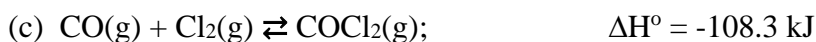
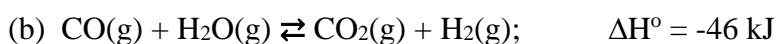
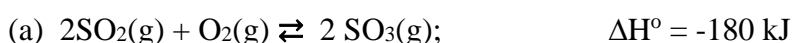
In chemical kinetics we learn that catalysts speed up reaction rates, but catalysts do not affect equilibrium.

Exercises-4:

1. Determine whether the following reactions favor high or low pressures?



2. Determine whether the following reactions favors high or low temperature?



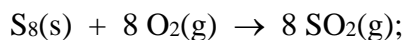
Some Industrially Important Chemical Equilibrium

Many important processes in chemical industries involve shifting equilibria to make the most of product at the lowest cost. The following are some of the examples.

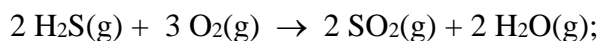
1. Contact Process for Sulfuric Acid

The production of sulfuric acid starts with the formation of sulfur dioxide, SO₂, formed:

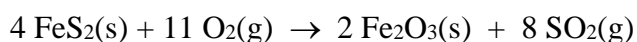
(1) by burning sulfur in dry air:



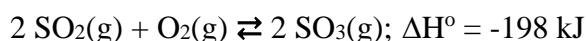
(2) from the combustion of hydrogen sulfide:



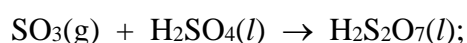
or (3) from the roasting processes of metal sulfides such as FeS₂ and FeCuS₂:



The next step, in the *contact process*, sulfur dioxide is converted to sulfur trioxide (SO₃) according to the following equation, which is exothermic and reversible:



The forward reaction favors high pressure but low temperature. However, at low temperature the reaction is very, very slow because the reaction has a very activation energy. The reaction is normally carried out at temperature between 400 - 500 °C and in the presence of catalyst. Increasing the temperature much higher will speed up reaction, but lowers the product yield. Thus, the temperature condition is compromised - high enough to make the reaction proceeds at a reasonable rate but low enough that it give a reasonable yield. The reaction is also driven in the forward direction, favoring the formation of SO₃, by continuously adding SO₂ and O₂ and simultaneously removing SO₃. Product formation is also favored by carrying out the reaction at high pressure. The SO₃ gas is dissolved in liquid (concentrated) sulfuric acid to form disulfuric acid, H₂S₂O₇, which is then reacted with water to form sulfuric acid:



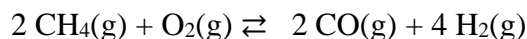
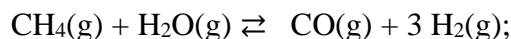
2. The Haber-Bosch Process for the Production of Ammonia

In the Haber-Bosch process, nitrogen and hydrogen gases are fixed to form ammonia:



The reaction is carried out at temperature about 250 °C and pressure 200-300 atm. Iron is used as catalyst to speed up the reaction. By mixing the reactants in stoichiometric proportions of nitrogen and hydrogen (that is, 1 volume of N₂ to 3 volume of H₂) and carrying out the reaction at high pressure, the percent yield of ammonia is between 15 - 20%. However, equilibrium is shifted to the right by adding more N₂ and H₂ gases and simultaneously removing the ammonia as it is formed. Ammonia condenses to a liquid under conditions at which nitrogen and hydrogen exist as gases. The unreacted nitrogen and hydrogen are recycled, together with the newly added batch of reactants.

In the above process, hydrogen is obtained from natural gas by the following reactions:



3. Production of Lime

Lime is produced by heating calcium carbonate:



The reaction is carried out at high temperature (900 - 1000 °C) and the equilibrium is shifted to the right by continuously removing the CO₂ gas. Lime is used for making mortar and plasters and as a cheap base in industry; it is used for treating acidic soil and in basic metal processing; Lime is also one of the ingredients in the manufacture of glasses and used in water purification.

Additional Exercises on Chemical Equilibrium

1. For the equilibrium: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$, $K_c = 4.60 \times 10^{-3}$ at 25°C.

If 0.0250 mole of N_2O_4 is initially placed in a 0.500-L flask, what would be the concentrations of N_2O_4 and NO_2 , respectively, when equilibrium is established?

- For the reaction: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$,
 $K_c = 49.7$ at 458°C . If the reaction mixture initially contains 0.500 M each of H_2 and I_2 , but no HI , what are the concentrations of the components at equilibrium at 458°C .
- Solid NH_4HS is introduced into an evacuated flask at 24°C and the following reaction takes place until equilibrium is attained:



At equilibrium the total pressure (for NH_3 and H_2S taken together) is 0.614 atm.

Calculate K_p for this equilibrium at 24°C .

- A 0.831-g sample of SO_3 is placed in an evacuated 1.00-L container and heated to 1100K. The SO_3 decomposes to SO_2 and O_2 as follows:



At equilibrium the total pressure in the container is 1.300 atm. Determine the value of the equilibrium constant K_p for this reaction at 1100 K.

EFFECT OF TEMPERATURE ON EQUILIBRIUM VAN'T HOFF'S EQUATION AND ITS INTEGRATION:

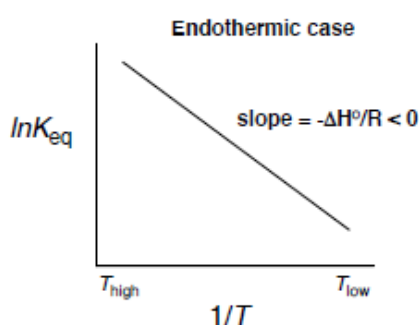
The van't Hoff equation provides information about the temperature dependence of the equilibrium constant. The van't Hoff equation may be derived from the Gibbs-Helmholtz equation, which gives the temperature dependence of the Gibbs free energy. For the standard Gibbs free energy, the Gibbs-Helmholtz equation is

$$\left(\frac{\partial \left(\frac{\Delta G^\circ}{T} \right)}{\partial \left(\frac{1}{T} \right)} \right)_P = \Delta H^\circ$$

Substituting the expression $\Delta G^\circ = -RT \ln K_{eq}$ and dividing both sides by $-R$, the first form of the van't Hoff equation is obtained,

$$\left(\frac{\partial \ln K_{eq}}{\partial \left(\frac{1}{T} \right)} \right)_P = -\frac{\Delta H^\circ}{R}$$

From this form of the van't Hoff equation, we see that at constant pressure, a plot with $\ln K_{eq}$ on the y-axis and $1/T$ on the x-axis has a slope given by $-\Delta H^\circ/R$. This is the origin of LeChatelier's Principle for the heat absorbed or evolved during the course of a chemical reaction. For an endothermic reaction, the slope is negative and so as the temperature increases, the equilibrium constant increases.

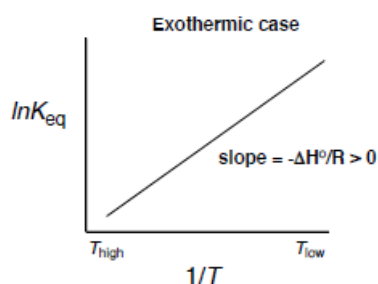


Typical van't Hoff plot for an endothermic reaction

An example endothermic reaction may be written in the following form,



For such a reaction, LeChatelier's Principle predicts that if the temperature increases, the system must shift to the right in order to alleviate the stress of additional heat. A shift to the right leads to an increase in products and a decrease in reactants, which increases the equilibrium constant as predicted by the van't Hoff equation. For an exothermic reaction, the slope is positive and so as temperature increases, the equilibrium constant decreases.



Typical van't Hoff plot for an exothermic reaction.

An example exothermic reaction may be written in the following form



For this type of reaction, LeChatelier's Principle predicts that if the temperature increases, the system must shift to the left in order to alleviate the stress of additional heat. A shift to the left leads to a decrease in products and an increase in reactants, which decreases the equilibrium constant as predicted by the van't Hoff equation.

An integrated form of the van't Hoff equation may be obtained at constant pressure

$$\begin{aligned}d \ln K_{eq} &= -\frac{\Delta H^\circ}{R} d(1/T) \\ \int_1^2 d \ln K_{eq} &= -\frac{\Delta H^\circ}{R} \int_1^2 d(1/T) \\ \ln K_2 - \ln K_1 &= -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)\end{aligned}$$

The integral on the right side was obtained assuming that the standard molar enthalpy of reaction is constant over the temperature range. Combining the natural logs, the integrated form of the van't Hoff equation is

$$\boxed{\ln \left(\frac{K_2}{K_1} \right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

Finally, an additional linear form of the van't Hoff equation may be obtained starting from the relation

$$\Delta G^\circ = -RT \ln K_{eq}$$

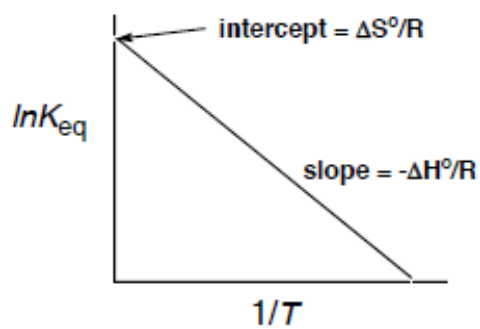
$$\ln K_{eq} = -\frac{\Delta G^\circ}{RT}$$

At any given temperature, the change in Gibbs free energy may be written from the definition of the Gibbs free energy as

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

Hence,
$$\ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

This equation indicates that a plot with $\ln K_{eq}$ on the y -axis and $1/T$ on the x -axis has a slope given by $-\Delta H^\circ/R$ and an intercept given by $\Delta S^\circ/R$. Note that in this figure, the slope is drawn for an endothermic reaction for example purposes.



MODULE-III

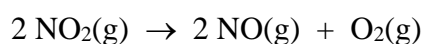
Chemical Kinetics is the study of reaction rates; that is, how fast a given reaction does proceeds. It is a measure of the change of the concentration of reactants (or products) as a function of time. Reaction rates provide information regarding how fast a chemical process occurs as well as the mechanism by which a reaction occurs at molecular level.

REACTION RATES

The rate of reaction is a measure of the change in concentration of reactants or products over time. Rate can be measured at the beginning of the reaction, which is called the *initial rate*, at any point in time while the reaction is in progress, called *instantaneous rate*, or over an interval of time, which is the *average rate*. In the *initial rate* the change in concentration of a reactant or product as a function of time is measured within minutes (or seconds) the reaction starts. Determination of the dependence of *initial rate* to the concentrations of reactants allows one to derive the *rate law* for the reaction. A *rate law* is a mathematical equation that shows the dependence of reaction rate to the molar concentrations of reactants at constant temperature. The *instantaneous rate* is calculated from the slope of a *tangent* drawn at any points on the *graph of concentrations versus time*. The slope of tangent taken at the initial point of the graph is assumed to be equal to its *initial rate*.

The *average rate* of reaction is obtained by dividing the change in concentration of a reactant or product that occurs over a longer period of time by the time interval that the change occurs.

For example, consider the following reaction at 300°C:



If in the first 150 seconds, the concentration of NO_2 has decreased from 0.0100 mol/L to 0.0055 mol/L, the average rate for the disappearance of NO_2 for first 150 s under this condition is,

$$\frac{-\Delta[\text{NO}_2]}{\Delta t} = \frac{-(0.0055 \text{ mol/L} - 0.0100 \text{ mol/L})}{150 \text{ s}} = \frac{0.0045 \text{ mol/L}}{150 \text{ s}} = 3.0 \times 10^{-5} \text{ mol/(L.s)}$$

Suppose that in the next 150 seconds the concentration of NO₂ decreases from 0.0055 mol/L to 0.0038 mol/L. The average rate during the second 150 s period is

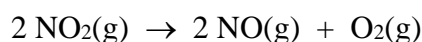
$$\frac{-\Delta[\text{NO}_2]}{\Delta t} = \frac{-(0.0038 \text{ mol/L} - 0.0055 \text{ mol/L})}{150 \text{ s}} = \frac{0.0017 \text{ mol/L}}{150 \text{ s}} = 1.1 \times 10^{-5} \text{ mol/(L.s)}$$

The *average rate* is the *mean* of several *instantaneous rates* taken over a period of time.

Note that *instantaneous rates* of a reaction decreases as time progresses as the concentrations of reactants decrease. Then the average rate taken over a longer period would have a smaller value compared to those taken over a shorter period after the reaction begins.

How is the rate of reaction measured?

The rate of reaction may be determined by measuring the rate of disappearance (decrease in concentration) of one of the reactants or the rate of formation (increase in concentration) of a product. For example, in the reaction:



Various expression of rate can be derived, such as

$$\text{Rate}_1 = \frac{-\Delta[\text{NO}_2]}{\Delta t}; \quad \text{Rate}_2 = \frac{\Delta[\text{NO}]}{\Delta t}; \quad \text{or} \quad \text{Rate}_3 = \frac{\Delta[\text{O}_2]}{\Delta t}$$

The stoichiometric relationships between the different rates are as follows:

$$\frac{-\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{NO}]}{\Delta t} = \frac{2\Delta[\text{O}_2]}{\Delta t}$$

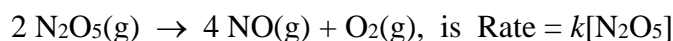
That is, in this reaction the rate of appearance of NO is the same as the rate of disappearance of NO₂, but double the rate of appearance of O₂.

RATE LAWS:

Consider a general reaction: $\text{A} + \text{B} \rightarrow \text{C}$

The rate law is expressed as, $\text{Rate} = k[\text{A}]^x[\text{B}]^y$,

where k is the rate constant; x and y are the *rate orders* with respect to individual reactants. The sum of the powers is called the **overall order**. The rate orders x and y are not related to the reaction coefficients. Their values must be experimentally determined from a set of kinetic data. For example, the rate law for reaction:



That is, the rate of the decomposition of N_2O_5 is *first order* with respect to $[\text{N}_2\text{O}_5]$, which means that the rate will double if $[\text{N}_2\text{O}_5]$ is doubled; it will triple if $[\text{N}_2\text{O}_5]$ is tripled.

For the reaction: $2 \text{NO}_2(\text{g}) \rightarrow 2 \text{NO}(\text{g}) + \text{O}_2(\text{g})$, the rate law is $\text{Rate} = k[\text{NO}_2]^2$.

That is, the rate of the decomposition of NO_2 is *second order* with respect to $[\text{NO}_2]$. Therefore, the rate will quadruple if $[\text{NO}_2]$ is doubled.

The reaction: $2 \text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ is found to be a zero order reaction in the presence of gold catalyst. For this reaction, the rate is independent of $[\text{HI}]$.

The Graphical Method for determining Zero-order, First-order and Second-order Rates

Consider a reaction: $\text{R} \rightarrow \text{Products}$.

(i) If the reaction is *zero-order* with respect to R, $\text{Rate} = \frac{-\Delta[\text{R}]}{\Delta t} = k$

This gives $\Delta[\text{R}] = -k\Delta t$, and $[\text{R}]_t = [\text{R}]_0 - kt$;

a plot of $[\text{R}]$ versus t yields a straight line with slope = $-k$

(ii) If the rate is *first-order* in $[\text{R}]$, $\text{Rate} = \frac{-\Delta[\text{R}]}{\Delta t} = k[\text{R}]$, which also gives $\frac{\Delta[\text{R}]}{[\text{R}]} = -k\Delta t$,

Integrating this equation from time $t = 0$ to $t = t$, yields the expression: $\ln[\text{R}]_t = \ln[\text{R}]_0 - kt$;

or $\ln([\text{R}]_t/[\text{R}]_0) = -kt$; If the common log is used, the integrated expression for first rate would be:

$\log[\text{R}]_t = \log[\text{R}]_0 - kt/2.30$; where, $[\text{R}]_0$ = concentration at $t = 0$, and $[\text{R}]_t$ = concentration at time t .

Plotting $\ln[R]_t$ versus t yields a straight line with slope = $-k$; (slope = $-k/2.30$ if $\log[R]_t$ is plotted).

(iii) If the rate is *second-order* with respect to R, $Rate = \frac{-\Delta[R]}{\Delta t} = k[R]^2$ or $\frac{\Delta[R]}{[R]^2} = k\Delta t$;

Integrating the equation from time $t = 0$ to $t = t$ yields the expression: $\frac{1}{[R]_t} = kt + \frac{1}{[R]_0}$

For second order rate, plotting $1/[R]_t$ versus t yields a straight line with the slope = k (the *rate constant*)

Half-Life of Reactions

The *half-life* ($t_{1/2}$) of a reaction is the time it takes for the reactant concentration to decrease to one-half its initial value.

For *zero-order* reaction, $t_{1/2} = [R]_0/2k$

For *first-order* reaction, $t_{1/2} = 0.693/k$

For *second-order* reactions, $t_{1/2} = 1/(k[R]_0)$

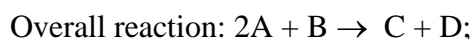
REACTION MECHANISM:

A **reaction mechanism** is the detailed picture of how a reaction occurs at molecular level. It consists of a *set of proposed elementary steps* involving molecular species – reactants as well as reaction *intermediates*. A reaction mechanism explains how a given reaction might occur at molecular level and from which a rate law can be derived, which must agree with the one determined experimentally. If the mechanism consists of more than one *elementary step*, the sum of these *steps* must be equal to the overall balanced equation for the reaction.

For example, the reaction: $2A + B \rightarrow C + D$ may involve the following *elementary steps*:

Step-1: $A + B \rightarrow X$;

Step-2: $X + A \rightarrow Y$;



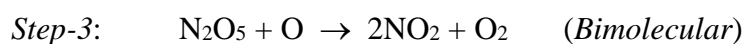
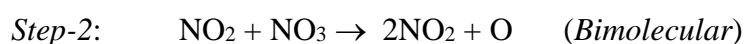
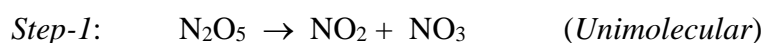
Elementary Steps and Molecularity

Elementary steps or *elementary reactions* are *simple* steps that together make up the *reaction mechanism* for a given reaction. Each *elementary reaction* describes *individual molecular event*, such as two particles combining or a particle (simple or complex) decomposing. An *elementary reaction* is characterized by its **molecularity**, which is the number of particles/molecules involved in the formation of *transition-state complex*. Thus, an elementary reaction may be characterized as *unimolecular*, *bimolecular*, or *termolecular*. Unimolecular and bimolecular reactions are considered the most common elementary processes.

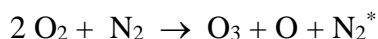
Rate Law for Elementary Reaction Steps:

Elementary Reactions	Molecularity	Rate Law
$A \rightarrow \text{product}$	Unimolecular	Rate = $k[A]$
$2A \rightarrow \text{product}$	Bimolecular	Rate = $k[A]^2$
$A + B \rightarrow \text{product}$	Bimolecular	Rate = $k[A][B]$
$2A + B \rightarrow \text{product}$	Termolecular	Rate = $k[A]^2[B]$

For example, in the reaction: $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$, the proposed mechanism is:



Termolecular event is considered very rare; the chances that three particles colliding at the same time, with proper orientation and sufficient energy, are considered extremely small. A possible *termolecular* event is thought to occur during the formation of ozone from oxygen in the outer atmosphere:



Deriving Rate Law from the Rate-Determining Step

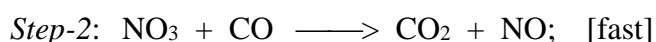
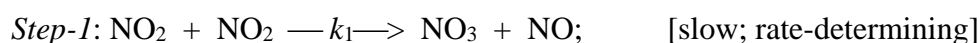
When a proposed mechanism consists of more than one elementary steps, the one with the slowest rate will determine the overall rate of reaction. It is called *the rate-determining step*, which *step represents the rate law for the overall reaction*.

Consider the reaction: $\text{NO}_{2(\text{g})} + \text{CO}_{(\text{g})} \rightarrow \text{NO}_{(\text{g})} + \text{CO}_{2(\text{g})}$

If the reaction follows a *one elementary step* mechanism, the rate law would be: $\text{Rate} = k[\text{NO}_2][\text{CO}]$

However, the experimentally determined rate law is $\text{Rate} = k[\text{NO}_2]^2$

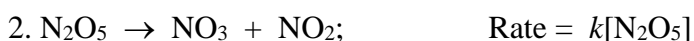
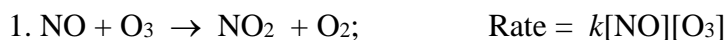
It is proposed that the reaction must involve at least *two elementary steps*:



The rate law for the rate-determining step: $\text{Rate} = k_1[\text{NO}_2]^2$, which is identical in form to the rate law obtained experimentally, in which $k_1 = k$. The second step, which occurs very fast, does not influence the overall rate.

In fact, if the exponents in the rate law differ from the coefficients in the chemical equation, the mechanism for the reaction normally involves more than one elementary step. Most reactions are believed to involve more than one elementary step.

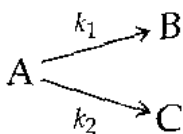
Note that, unlike the overall rate law which must be determined experimentally, the rate law for an *elementary reaction* can be deduced from its *molecularity*, since each elementary reaction is a single step event. The exponents in the expression of rate law are the same as the equation coefficients. For example, the rate laws for the following elementary reactions are written as indicated:



In addition, certain species such as NO_3 may be formed in one *elementary step*, but immediately consumed in subsequent elementary step; they do not appear in the overall equation. These species are called *reaction intermediates*.

COMPLEX REACTIONS:

PARALLEL REACTIONS: Consider following reaction:



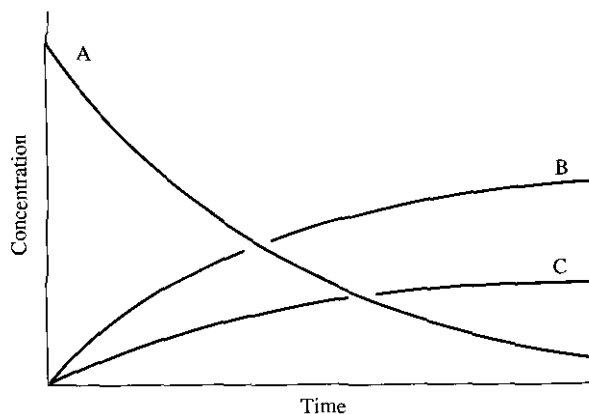
We can write simple rate equations to describe the process:

$$-\frac{d[\text{A}]}{dt} = k_1[\text{A}] + k_2[\text{A}] = (k_1 + k_2)[\text{A}]$$

$$\frac{d[\text{B}]}{dt} = k_1[\text{A}]$$

$$\frac{d[\text{C}]}{dt} = k_2[\text{A}]$$

The first equation is similar to first order reaction and can be integrated readily. Once the time dependence of disappearance of A is known, we can substitute it in the remaining equations to calculate their concentration dependence.



$$\ln \frac{[A]}{[A]_0} = -(k_1 + k_2)t$$

$$[A] = [A]_0 \exp[-(k_1 + k_2)t]$$

$$\frac{d[B]}{dt} = k_1[A] = k_1[A]_0 \exp[-(k_1 + k_2)t]$$

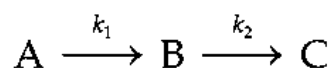
$$\frac{d[C]}{dt} = k_2[A] = k_2[A]_0 \exp[-(k_1 + k_2)t]$$

$$[B] = \frac{k_1[A]_0}{k_1 + k_2} \{1 - \exp[-(k_1 + k_2)t]\}$$

$$[C] = \frac{k_2[A]_0}{k_1 + k_2} \{1 - \exp[-(k_1 + k_2)t]\}$$

CONSECUTIVE REACTIONS:

Consider a simple consecutive reaction



As before, we can write the kinetic rate equations for such a scheme.

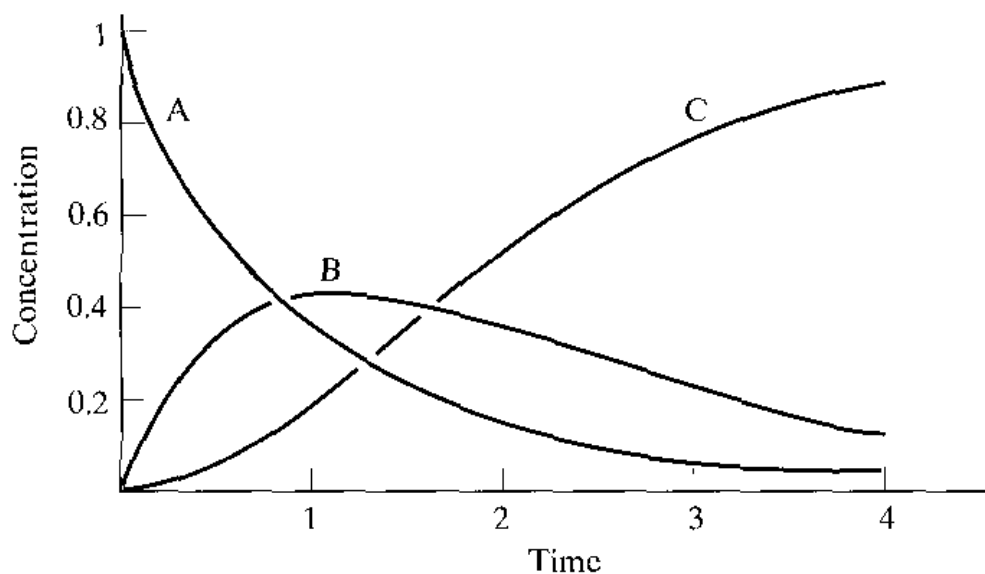
$$-\frac{d[A]}{dt} = k_1[A] \quad \frac{d[B]}{dt} = k_1[A] - k_2[B] \quad \frac{d[C]}{dt} = k_2[B]$$

The solution for the first equation is simple but for B and C is bit more complex.

$$[A] = [A]_0 \exp(-k_1 t)$$

$$[B] = \frac{k_1[A]_0}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)]$$

$$[C] = [A]_0 \left\{ 1 - \frac{1}{k_2 - k_1} [k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \right\}$$



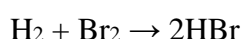
CHAIN REACTIONS:

Chain reactions are complex reactions that involve *chain carriers*, reactive intermediates which react to produce further reactive intermediates. The elementary steps in a chain reaction may be classified into *initiation*, *propagation*, *inhibition*, and *termination* steps.

The hydrogen-bromine reaction has become the ‘benchmark’ system for illustrating the kinetics of linear chain reactions, and we will use this reaction as our main example. We will also compare the kinetics of the hydrogen-bromine reaction with the analogous reactions of chlorine and iodine.

The hydrogen – bromine reaction

The kinetics of the reaction between H₂ and Br₂ were determined experimentally by Bodenstein around 100 years ago. The overall reaction has the equation



Bodenstein determined the following rate law for the reaction:

$$d[\text{HBr}]/dt = k [\text{H}_2][\text{Br}_2]^{1/2}$$

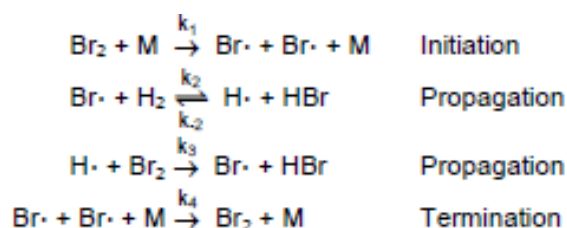
The measured order of 1/2 with respect to Br₂ indicated that the reaction proceeded via a complex reaction mechanism rather than a simple bimolecular collision. Further investigation showed that this rate law in fact only holds for the early stages of the reaction, and that the true rate law takes the form:

$$d[\text{HBr}]/dt = (k [\text{H}_2][\text{Br}_2]^{1/2}) / (1 + k' [\text{HBr}]/[\text{Br}_2])$$

Any proposed mechanism for the reaction must agree with both of these observations. The reaction can be initiated by either thermally-induced or photon-induced dissociation of Br₂.



We will concentrate on the thermal mechanism for the purposes of deriving a rate law for the overall reaction, but the steps following the initiation step are the same for both cases. The currently accepted mechanism is:



The reaction chain contains two radical chain carriers, H. and Br.. In the second step, because the H-H bond is stronger than the H-Br bond, once an appreciable amount of HBr has built up the reverse (inhibition) reaction becomes possible. In order to arrive at an overall rate law for the reaction, we apply the steady state approximation to the two chain carriers.

$$\frac{d[H]}{dt} = 0 = k_2[Br][H_2] - k_{-2}[H][Br] - k_3[H][Br_2]$$

$$\frac{d[Br]}{dt} = 0 = 2k_1[Br_2][M] - k_2[Br][H_2] + k_{-2}[H][HBr] + k_3[H][Br_2] - 2k_4[Br]^2[M]$$

We can solve these two equations to obtain expressions for the concentrations of H and Br in terms of the reactant and product concentrations and the various rate constants. The two equations each depend on both carrier concentrations, and also share terms. We can simplify the equations by adding them together to give:

$$0 = 2k_1[Br_2][M] - 2k_4[Br]^2[M]$$

which can be rearranged to give the steady state concentration of Br atoms.

$$[Br] = \left(\frac{k_1[Br_2]}{k_4} \right)^{1/2}$$

This implies that the rate of initiation is the same as the rate of termination, as expected under steady state conditions (this is a good check that we have made no mistakes up to this point).

This result also leads to a considerable simplification, which now becomes

$$0 = -k_2[Br][H_2] + k_{-2}[H][HBr] + k_3[H][Br_2]$$

and may be rearranged to give an expression for the steady state H atom concentration.

$$[H] = \frac{k_2[Br][H_2]}{k_{-2}[HBr] + k_3[Br_2]} = \frac{k_2[H_2]}{k_{-2}[HBr] + k_3[Br_2]} \left(\frac{k_1[Br_2]}{k_4} \right)^{1/2}$$

We are now ready to determine the overall reaction rate.

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] - k_{-2}[H][HBr] + k_3[H][Br_2]$$

Substituting in our expressions for [H] and [Br] gives

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_2(k_1/k_4)^{1/2}[\text{Br}_2]^{1/2}[\text{H}_2]}{1 + (k_2/k_3)[\text{HBr}]/[\text{Br}_2]}$$

We see that this agrees with the measured rate law. In the early stages of the reaction, the concentration of the HBr product is much lower than that of the reactant Br₂, and the second term in the denominator becomes negligible. The rate law then reduces to

$$\frac{d[\text{HBr}]}{dt} = 2k_2(k_1/k_4)^{1/2}[\text{Br}_2]^{1/2}[\text{H}_2]$$

again reproducing the experimental observations. The proposed mechanism therefore fits well with the experimental measurements.

COLLISION THEORY:

As the name suggests, simple collision theory represents one of the most basic attempts to develop a theory capable of predicting the rate constant for an elementary bimolecular reaction of the form $A + B \rightarrow P$. We begin by considering the factors we might expect a reaction rate to depend upon. Obviously, the rate of reaction must depend upon the rate of collisions between the reactants. However, not every collision leads to reaction. Some colliding pairs do not have enough energy to overcome the activation barrier, and any theory of reaction rates must take this energy requirement into account. Also, it is highly likely that reaction will not even take place on every collision for which the energy requirement is met, since the reactants may need to collide in a particular orientation (e.g. SN₂ reactions) or some of the energy may need to be present in a particular form (e.g. vibration in a bond coupled to the reaction coordinate). In summary, there are three aspects to a successful reactive collision, and we might expect an expression for the rate of a bimolecular reaction to take the following form.

$$v = (\text{encounter rate}) (\text{energy requirement}) (\text{steric requirement})$$

We will now consider each of these factors in more detail.

1. Encounter rate

We showed in the ‘Properties of gases’ lecture course that the rate of collisions between molecules A and B present at number densities n_A and n_B is

$$Z_{AB} = \sigma_C \left(\frac{8kT}{\pi\mu} \right)^{1/2} n_A n_B = \sigma_C \left(\frac{8kT}{\pi\mu} \right)^{1/2} N_A^2 [A][B]$$

2. Energy requirement

For a Maxwell-Boltzmann distribution of molecular speeds, the fraction of collisions for which the energy is high enough to overcome the activation barrier is $\exp(-E_a/RT)$.

3. Steric requirement

Experimentally, measured rates are often found to be up to an order of magnitude smaller than those calculated from simple collision theory, suggesting that features such as the relative orientation of the colliding species is important in determining the reaction rate. We account for the disagreement between experiment and theory by introducing a steric factor, P , into our expression for the reaction rate. Alternatively, we can replace the collision cross section, σ_C , with a reaction cross section σ_R , where $\sigma_R = P\sigma_C$. Usually, P is considerably less than unity, but values greater than one are also possible. An example is the ‘harpoon reaction’ between Rb and Cl_2 . The reaction mechanism involves an electron transfer at large separations to form $\text{Rb}^+ + \text{Cl}_2^-$, after which the electrostatic attraction between the two ions guarantees reaction. P is large because the reaction cross section is determined by the electron transfer distance, which is much larger than the collision diameter.

Combining these three terms, the simple collision theory expression for the reaction rate is:

$$v = P \sigma_C \left(\frac{8kT}{\pi\mu} \right)^{1/2} \exp\left(\frac{-E_a}{RT}\right) n_A n_B$$

and we can identify the second order rate constant as

$$v = P \sigma_C \left(\frac{8kT}{\pi\mu} \right)^{1/2} \exp\left(\frac{-E_a}{RT}\right)$$

Simple collision theory provides a good first attempt at rationalising the Arrhenius temperature dependence seen for many reaction rate constants. However, at a quantitative

level the predictions of the theory are far from accurate. There are a number of ways in which the model breaks down;

(i) It does not account for the fact that, unless the collision is head on, not all of the kinetic energy of the two reactants is available for reaction. Conservation of angular momentum means that only the kinetic energy corresponding to the velocity component along the relative velocity vector of the reactants actually contributes to the collision energy.

(ii) The energy stored in internal degrees of freedom in the reactants (vibrations, rotations etc) has been ignored. For reactions involving large molecules, this often leads to a large discrepancy between simple collision theory and experiment, though this is partly corrected for by the inclusion of the steric factor, P . This problem is largely solved in another theory known as transition state theory, which you will learn about next year.

ACTIVATION ENERGY AND TRANSITION STATE THEORY:

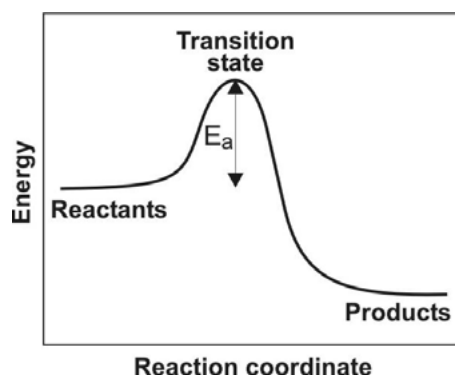
The rate law of a reaction relates the dependence of reaction rates on the concentrations of reactants. As we know, the rate of reaction also depends on other factors, such as temperature. This dependency can be explained by the *collisional theory* of reaction and the formation of *activated complex*, or *transition state*.

Consider the following reaction: $2\text{BrNO}(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{Br}_2(\text{g})$

For the reaction to occur:

- *Reactant molecules must collide;*
- *Molecular collisions must occur with proper orientations;*
- *Collisions must be energetic and lead to the formation of an activated complex;*
- *The rate of formation of activated complex is the rate determining step;*
- *The activated complex eventually leads to the formation of products;*

1. The rate of formation of *activated complex* is proportional to the *frequency of effective molecular collisions*, which is dependent on reactant concentrations.
2. The *activated complex* or *transition state* is separated from the reactants by an *energy barrier*, called the **activation energy (E_a)**. The formation of *transition state complex* depends on the fraction of molecules with sufficient *kinetic energy* that can overcome this *energy barrier*. This fraction is temperature dependent. At low temperature, the *fraction* of molecules with sufficient energy to overcome the *activation energy barrier* and subsequently forms the *transition state complex* will be low. This *fraction* increases with temperature, which also increase the overall reaction rate.
3. High *activation energy* for a reaction also means a lower fraction of molecules with sufficient energy to form the *transition state complex*. Thus, higher E_a leads to a slower rate of reaction.



The dependence of rate on temperature and *activation energy* (E_a) is shown the Arrhenius equation for the rate constant, k :

$$k = A e^{-E_a/RT}, \quad \text{where } A \text{ is called the Arrhenius frequency factor.}$$

Taking the natural log, yields the equation: $\ln(k) = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln(A)$.

A plot of $\ln(k)$ versus $1/T$ yields a straight line with slope = $-E_a/R$; ($R = 8.314 \text{ J/mol.K}$).

The *activation energy* (E_a) can also be calculated using two values of the rate constant k according to the expression:

$$\ln(k_2/k_1) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right); \text{ or } \ln(k_1/k_2) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right); \text{ (T must be in Kelvin)}$$

MODULE-IV

THERMODYNAMIC SYSTEMS:

The scope of thermodynamics

Thermodynamics is a phenomenological theory of matter. As such it draws its concepts directly from experiments. In its pure form it does not relate to the microscopic structure of matter (although such relations are made in *statistical thermodynamics*). Thermodynamics relate to time scales much longer than molecular vibrations or collision rates, and dimensions much larger than atomic sizes. Historically it has evolved before detailed understanding of the microscopic nature of material was realized.

The thermodynamic system and its walls.

The *thermodynamic system* is any macroscopic system. Its walls define restriction on the system. They can prevent flow of heat (*adiabatic*) material (*a closed system*) or changes in the volume or pressure. A *thermodynamic state* is specified by a set of *thermodynamic parameters (or coordinates)* necessary for the description of the system. These parameters are measurable quantities associated with the system (*i.e. p-pressure V-volume H-magnetic field*)

These parameters may be *extensive* namely proportional to the size of the system (*i.e. V, n, internal energy*) or *intensive*- independent on the size (*i.e. p, T, C_v, C_p, x_i*)

The thermodynamic equilibrium.

The *thermodynamic equilibrium* prevails when a state of the system does not change in time, under the conditions of unchanging walls. Note however:

- The equilibrium is relative (*diamond and graphite; H₂ + O₂ H₂O; He + D₂ and fusion*)

- Microscopically it is dynamic- (*there are always fluxes and decaying fluctuations*)
- Sometimes stable states are not in equilibrium (*barriers for change*)
- There are many components for the equilibrium: (*mechanical-pressure or forces, Thermal-temperature, chemical*)

The equation of state.

The equation of state is a functional relationship among the thermodynamic parameters for a system in equilibrium $f(p, V, T, \{n_i\}) = 0$; Generally, it relates to all phases. The composition of a system can be given in moles, mole fraction, or concentration. i.e. the equation of state of the ideal gas in a *single component* system:

$$pV - nRT = 0; \text{ or } pV - RT = 0; R = 8.3143 \text{ J K}^{-1} \text{ mole}^{-1} \text{ or } 1.986 \text{ cal K}^{-1} \text{ mole}^{-1} \text{ or } 0.082 \text{ l atm K}^{-1} \text{ mole}^{-1}$$

Consider the following properties derived from the equation of state:

1. Volume expansion coefficient: $\alpha = V^{-1} (\partial V / \partial T)_P$: for ideal gases equals $1/T$
2. Compressibility: $\kappa = -V^{-1} (\partial V / \partial P)_T$: for ideal gases equals $1/P$ (sometimes marked β)

Two specific points in equation of state should be emphasized: A. ***The triple point*** where the solid liquid and gaseous phases coexist in equilibrium. B. ***The critical point*** where there is continuous transition between liquid and gas. At the critical point κ diverges to infinity. $Z = \sim 0.3$ at this point. While the equation defines the state, not all properties can be extracted from it.

The zeroth law

The law deals with the nature of thermal equilibrium, when two systems are brought to thermal contact:

Two bodies which are each in thermal equilibrium with a third body, are in thermal equilibrium with each other

The conclusion is that all bodies in thermal equilibrium have a common property: temperature (*similar in properties to electric potential*). The experimental temperature will be measured by using a standard system which one of its properties will be used to define the experimental temperature.

i.e. : expansion of a body (*mercury*), pressure of a gas in constant volume or the volume under constant pressure conditions. In the case of ideal gas $T = pV/R$ where V is the molar volume.

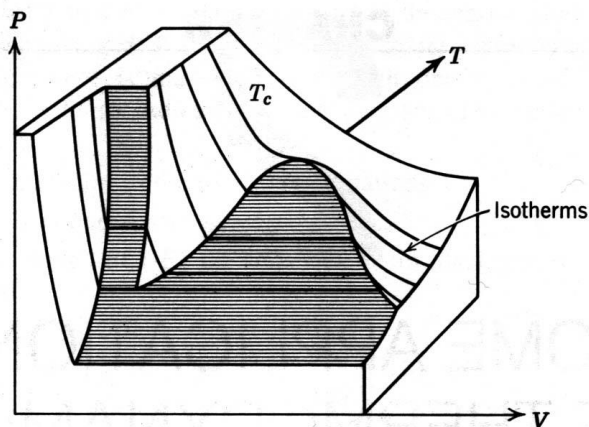
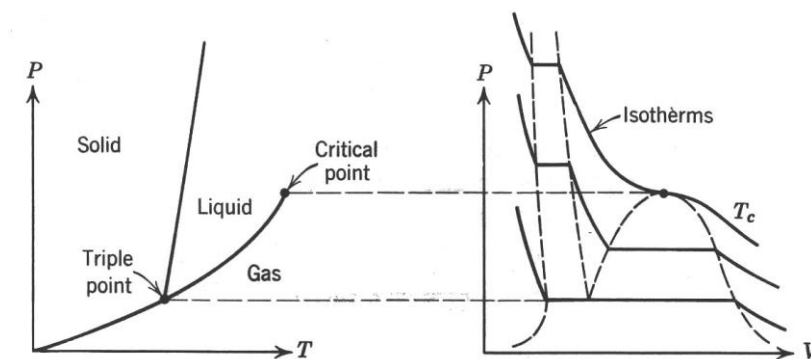


Fig. 2.1 Surface of equation of state of a typical substance (not to scale).

Not always is the temperature related to mechanical property (*the conductivity of a metal, semiconductor, the light emission of “a black body”*)

Real gases and their equations of state.

The equation of state for ideal gases fails to describe the behavior of real gases. Deviations are notable at high pressures and low temperatures. At high pressures molecules are pushed close together and a significant fraction of the volume is occupied by the molecules themselves. At low temperatures, namely low kinetic energies of the molecules, the interaction between molecules influences the pressure. Deviations from the ideal-gas behavior is conveniently expressed by the **compressibility factor** $Z = pV/RT$. Note that for ideal gas $Z=1$.



- A. different gases are characterized by different Z functions. (He is more "ideal" than N_2)
- B. Deviation of Z from 1 may be negative at low pressures (molecular attraction effect), but are always positive at very high pressures (finite volume effects)
- C. At higher temperatures the negative deviations disappear.

The virial equation:

More elaborate equations of states have to be formulated in order to account for the behavior of real gases. The virial equation expresses the compressibility factor as a power series of $1/V$ for a pure gas (note that $1/V$ is proportional to the density)

$$Z = pV/RT = 1 + B/V + C/V^2 + \dots$$

B and C are referred to as the second and third virial coefficients. They are specific to the gas and depend on the temperature. For many purposes it is more convenient to have the pressure as the independent variable and write the virial equation as:

$$Z = pV/RT = 1 + B'p + C'p^2 + \dots$$

It can be shown that $B' = B/RT$ and $C' = (C - B^2)/(RT)^2$

For each gas there is a temperature at which B is zero. It is called the **Boyle temperature**. (for nitrogen 54 C) At this temperature the gas behaves as an ideal gas over an extended pressure range.

THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is a statement of the law of energy conservation by using a new thermodynamic state function the internal energy. In general, along history, the adherence to the principle of energy conservation have led to the discovery of new forms of energy: (i.e. $1/2 mv^2 + mgh$, coulombic energy, relativity)

Thermodynamic processes.

In a **thermodynamic process or transformation** the system moves from one equilibrium state to another. The transformation is **quasi-static** for slowly varying conditions, and is **reversible** if a system retraces its history in time if the external conditions retrace their history. Any reversible process is quasi-static (but not the opposite).

Work and heat and internal energy.

Let's examine several processes:

Mixing of liquids (only initial and final states are defined)

Adiabatic expansion or compression (trajectory is well defined) Work Performed on the system: $dW = -p_{\text{ext}} dV$. Where p_{ext} is the external pressure on the system.

Irreversible expansion (a jumping piston).

Other mechanical work: Rubber band expansion (the concept of work will be expanded to include non-mechanical work like electrical-work)

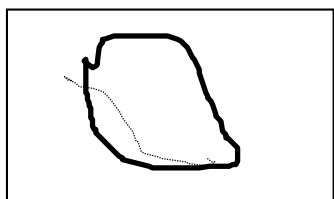
The Joule experiments (1843-1878) showed that under adiabatic condition there was a fixed ratio between the work done on the system and the increase in its temperature.

The same change in the state of a system (namely heating) could be done by contacting it with a *heat reservoir* (a body large enough to transfer heat without changing its temperature.). **Heat** absorbed by the system is defined as q .

The first law and internal energy

$\Delta U = q+w$; The change in the internal energy of a system is defined as the sum of work done on the system and the heat absorbed by it.

The difference in the internal energy between two states does not depend on the trajectory.



This law can be formulated in the following way:

$$\oint dU = 0; \quad \int_a^b dU = U_b - U_a$$

Additional conservation laws that we take as trivial are mass charge and atoms in closed systems (ignoring nuclear reactions).(examples: water, H_2 and O_2 , or inert solvent in chemical reaction)

In contrast to the internal energy, **work** or **heat** separately are not state functions. Heating only, or work only on the system can bring it to the same state.

Exact and inexact differentials

A function which is a state function should be exact. Its integration from state A to B should not depend on the path. The Euler criterion for such exactness is given by:

$$\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) = \frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) \quad \text{for } f=f(x,y) \text{ or:}$$

for $df = Mdx + Ndy$ where $M \equiv \partial f / \partial x$ and $N \equiv \partial f / \partial y$ f is exact if: $\partial M / \partial y = \partial N / \partial x$

Exercise: Show that the volume of the ideal gas is an exact function.

REVERSIBLE AND IRREVERSIBLE EXPANSION OF GASES:

Work of expansion

If a system (parcel) is not in mechanical (pressure) equilibrium with its surroundings, it will expand or contract. Consider the example of a piston/cylinder system, in which the cylinder is filled with a gas. The cylinder undergoes an expansion or compression as shown below. In p-V thermodynamic diagram, in which the physical state of the gas is represented by two thermodynamic variables: p,V in this case. [We will consider this and other types of thermodynamic diagrams in more detail later. Such diagrams will be used extensively in this course.] For the example below, every state of the substance is represented by a point on the graph. When the gas is in equilibrium at a state labeled P, its pressure is p and volume is V. If the piston of cross-sectional area A moves outward a distance dx while the pressure remains constant at p, the work dW (work is defined by the differential $dw \equiv f \cdot ds$) is

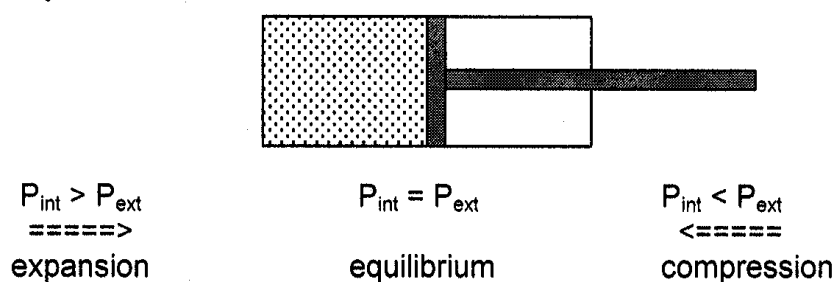
$$dW = pA dx = p dV \quad (\text{shaded region of the graph}).$$

The total work is found by integrating this differential over the initial and final volumes V_1

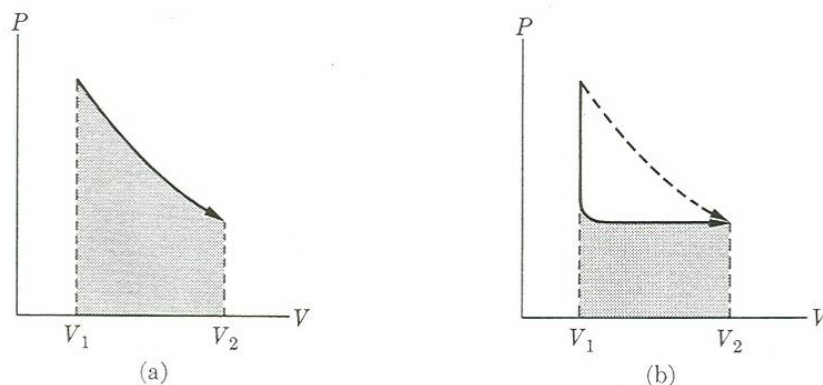
and V_2 : $W = \int_{V_1}^{V_2} p dV$

Reversible processes produce the maximum amount of work

If a process does work on the surroundings, you get more work out of the process if it is done slowly. This is because less heat is lost to the surroundings. So a reversible process (infinitely slow) does the maximum work. There is one example of this that is easy to understand: the work done by a gas expanding inside a piston. We will see that the maximum amount of work is obtained when the gas is allowed to expand very slowly (reversibly).



Let's compare a reversible vs. an irreversible expansion of the gas. Initially, let's assume that the internal and external pressures are the same ($P_{\text{int}} = P_{\text{ext}}$). To expand the gas reversibly, we reduce the external pressure very slowly (technically, infinitely slowly) so the system never strays significantly from equilibrium. This is a reversible process because a very small increase in the external pressure would cause the gas to be compressed. To expand the gas irreversibly, we reduce the pressure very quickly. As the gas expands it does work on the surroundings (by moving the piston against the external pressure). The plots of pressure vs. volume for these two processes are shown below. Figure (a) represents the reversible expansion. Figure (b) is the irreversible expansion.



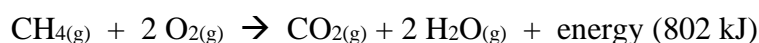
The work done in these two processes is the area under the curves. (Remember that PV has units of energy or work). Clearly, more work is done by the reversible expansion. The reversible expansion does the maximum amount of work because the gas is pushing against the maximum possible external pressure. (Since the process remains at equilibrium throughout the reversible expansion, $P_{\text{ext}} = P_{\text{int}}$.) If the external pressure was any higher, the process would reverse and the gas would be compressed.

In general, energy released by a reversible process can do the maximum amount of work because less of the energy is lost as heat. A process that is done quickly (irreversibly) tends to generate turbulence and friction resulting in heat loss to the surroundings.

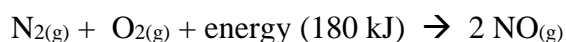
ENTHALPY AND CALORIMETRY

Chemical Energy

Chemical reactions are either *exothermic* (produce heat) or *endothermic* (absorb heat). The combustion of methane gas is an example of exothermic reaction:



The formation of nitrogen monoxide (NO) from nitrogen and oxygen is an endothermic reaction:



How much heat is produced or absorbed in a reaction will depend on the difference between the potential energy of the reactants and products.

Enthalpy

Enthalpy is heat of reaction measured at constant pressure. Like internal energy (E), enthalpy (H) is a *state function*. The enthalpy value (ΔH) depends only on the initial and final state and not on how the change occurs.

Enthalpy, H , is defined as $H = E + PV$;

and enthalpy change, $\Delta H = \Delta E + P\Delta V + V\Delta P$.

If the process occurs at constant pressure ($\Delta P = 0$), $V\Delta P = 0$, and

$$\Delta H = \Delta E + P\Delta V$$

From the expression of the first law of thermodynamics, if a process occurs at constant pressure,

$$\Delta E = q_p + W; \quad \rightarrow \quad q_p = \Delta E - W;$$

Since $W = -P\Delta V$, $\rightarrow \quad q_p = \Delta E + P\Delta V; \quad \rightarrow \quad \Delta H = q_p$.

Thus, *for a process at constant pressure, the enthalpy change (ΔH) for system is equal to the energy flow as heat*. Thus, for a reaction studied under constant pressure, the quantity of heat produced or absorbed by the system (the reaction) is the enthalpy change for the reaction.

For a process at constant volume, $\Delta V = 0$, $W = -P\Delta V = 0$, and $\Delta E = q$. That is, ΔE is the energy change for a process occurring at constant volume.

Calorimetry

A calorimeter is a device used for determining the heat of reaction. The simple “Styrofoam coffee-cup calorimeter” is often used in laboratories to measure the heat of reaction in aqueous solution, which occurs at constant pressure. This type of calorimeter measures the enthalpy change (ΔH) of a reaction. The heat produced by the reaction is absorbed by the solution (the

reaction's surrounding), which can be calculated from the mass, its specific heat, and the temperature change of the solution using the expression: $q_{\text{soln}} = m \times s \times \Delta t$

For example, suppose we mix 50.0 mL of 1.0 M HCl and 50.0 mL of 1.0 M NaOH in a coffee-cup calorimeter and both solution were initially at 22.0 °C. After mixing, the temperature of the solution rises to 29.0 °C. Assuming the density of the solution as 1.0 g/mL and the specific heat of the solution as 4.02 J/g.°C, the amount of heat absorbed by the solution is calculated as follows:

$$q_{\text{soln}} = 100.0 \text{ g} \times (4.02 \text{ J/g.}^\circ\text{C}) \times 7.0 \text{ }^\circ\text{C} = 2814 \text{ J} = 2.8 \times 10^3 \text{ J}$$

If the heat capacity of the calorimeter is known, let say $C_{\text{cal}} = 10.\text{J}/^\circ\text{C}$, we can also calculate the heat absorbed by the calorimeter, which is,

$$q_{\text{cal}} = (10. \text{ J}/^\circ\text{C}) \times 7.0 \text{ }^\circ\text{C} = 70. \text{ J}$$

The total heat produced by the reaction (q_{rxn}) is equal to the sum of the above heat absorbed by the solution and calorimeter:

$$q_{\text{rxn}} = -(q_{\text{soln}} + q_{\text{cal}}) = -(2814 \text{ J} + 70 \text{ J}) = -2884 \text{ J} = -2.9 \text{ kJ}$$

The reaction is: $\text{HCl}_{(\text{aq})} + \text{NaOH}_{(\text{aq})} \rightarrow \text{H}_2\text{O}_{(\text{l})} + \text{NaCl}_{(\text{aq})}$,

and the ionic equation is: $\text{H}^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \rightarrow \text{H}_2\text{O}_{(\text{l})}$

The number of mole of H^+ reacted = $0.0500 \text{ L} \times 1.0 \text{ mol/L} = 0.0500 \text{ mol}$

That is, 2.9 kJ of heat is produced when 0.0500 mol H^+ ions is reacted. The molar enthalpy for the reaction is $-2.9 \text{ kJ}/(0.0500 \text{ mol}) = -58 \text{ kJ/mol}$

A "bomb-calorimeter" is a type of calorimeter used to measure the amount of heat produced in a combustion reaction. It measures the heat of reaction carried out at constant volume. The amount of heat produced is calculated by measuring the heat absorbed by the calorimeter, which is

$$q_{\text{comb.}} = -q_{\text{cal}}; \quad \text{and} \quad q_{\text{cal.}} = C_{\text{cal}} \times \Delta t; \quad (C_{\text{cal}} = \text{heat capacity of the calorimeter})$$

HEAT CAPACITIES

Two heat capacities are derived from the above definitions:

$$C_V - \text{Heat capacity under constant volume conditions} \quad C_V \equiv \delta q_v / dT = (\partial U / \partial T)_V$$

$$C_p - \text{Heat capacity under constant pressure conditions} \quad C_p \equiv \delta q_p / dT = (\partial H / \partial T)_p$$

Both heat capacities are extensive variables, are extracted experimentally, and are function of temperature (*Recall the freezing of the degrees of freedom with temperature*). At a given state, C_p is always larger than C_V since in addition to increasing internal energy in the heating process work of expanding against external pressure is performed. (\underline{C}_p and \underline{C}_V , the molar heat-capacities, are intensive variables). The inverse conclusions are that the change in H as a function of temperature can be expressed as : $\Delta H = \int C_p dT$, and respectively the change in the internal energy $\Delta U = \int C_V dT$ over the relevant temperature range.

The relation between C_V and C_p :

Let us try now to estimate quantitatively the difference between the two heat capacities:

$$C_p - C_V = (\partial H / \partial T)_p - (\partial U / \partial T)_V = (\partial U / \partial T)_p + p(\partial V / \partial T)_p + \underbrace{V(\partial p / \partial T)_p}_{=0} - (\partial U / \partial T)_V$$

$$\text{Since } dU = (\partial U / \partial V)_T dV + (\partial U / \partial T)_V dT \Rightarrow (\partial U / \partial T)_p = (\partial U / \partial V)_T (\partial V / \partial T)_p + (\partial U / \partial T)_V$$

$$C_p - C_V = [p + (\partial U / \partial V)_T] (\partial V / \partial T)_p = [p + (\partial U / \partial V)_T] V \alpha \quad \text{where } \alpha \text{ is the thermal expansion coefficient.}$$

The ideal gases case:

The Joule experiments have shown that for an thermally isolated system of “practically” ideal gas $\Delta T = 0$ upon expansion to vacuum. (*an adiabatic irreversible expansion*). In the free expansion $w = 0$ (*since there was no external pressure*) and $q = 0$ (*thermally isolated*). The conclusion is that $\Delta U = 0$ in the free-expansion. The general conclusion is that, in a closed

system, since U is a state function it depends in ideal gas on the temperature only (*not on the volume*). Since $H=U+PV$, H is also a function of temperature only in ideal gases.

Therefore for ideal gases: $C_p - C_v = [p + (\partial U / \partial V)_T] V \alpha = nRT \alpha = nR$

Adiabatic reversible processes in gases

We wish to investigate the p-V relations in reversible *adiabatic expansion*; For this process $q = 0$. Let us assume that p-V is the only relevant work.

The adiabatic route can be decomposed to isochoric and isobaric trajectory:

$$\Delta U_{dac} = C_p \Delta T_{da} + p_d \Delta V + C_v \Delta T_{ac} =$$

$$\Delta U_{dc} \cong p_d \Delta V \quad [- \int p dV] \quad (\text{adiabatic trajectory})$$

Since U is a state function we compare these two expressions.

$$C_p \Delta T_{da} + p_d \Delta V + C_v \Delta T_{ac} = p_d \Delta V \Rightarrow C_p / C_v \equiv \gamma = -\Delta T_{ac} / \Delta T_{da}$$

but also, assuming equal spaces between isotherms of equal ΔT :

$$-\Delta T_{ac} / \Delta T_{da} = (\partial p / \partial V)_{\text{adia}} / (\partial p / \partial V)_T$$

$$(\partial p / \partial V)_{\text{adia}} / (\partial p / \partial V)_T = C_p / C_v \equiv \gamma$$

The ideal gases case:

It is easy to derive the expression directly for ideal gases.

Since U depends on temperature only for ideal gas, in the adiabatic reversible expansion:

$$dU = n C_v dT = -p dV = -nRT dV/V \Rightarrow C_v dT/T = -R dV/V \Rightarrow T^{(C_v / C_p - C_v)} V = \text{constant}$$

Naturally, our general formalism brings about the same results:

$$(\partial p / \partial V)_T = -nRT/V^2 = -p/V$$

$$(\partial p / \partial V)_{\text{adia}} = -C_p / C_v * p/V \equiv -\gamma p/V \Rightarrow pV^\gamma = \text{constant}; TV^{\gamma-1} = \text{constant} \dots\dots$$

THERMOCHEMISTRY

In chemistry we are often interested in energy exchange of chemical reactions and mostly in isobaric conditions. This makes the thermodynamic function enthalpy a very useful concept.

Consider the general chemical reaction: $\sum v_i A_i = 0$; i.e. The water formation reaction:

$H_2 + 1/2 O_2 = H_2O$ is written in this convention as: $-1 H_2 - 1/2 O_2 + 1 H_2O = 0$;

Consider the *extent of reaction* ξ defined as $n_i = n_{i0} + v_i \xi$

$$dH = \sum_{i=1}^N \bar{H}_i dn_i = d\xi \sum_{i=1}^N v_i \bar{H}_i$$

KIRCHOFF EQUATION

Kirchoff relation predicts the effect of temperature on the latent heat of phase transition.

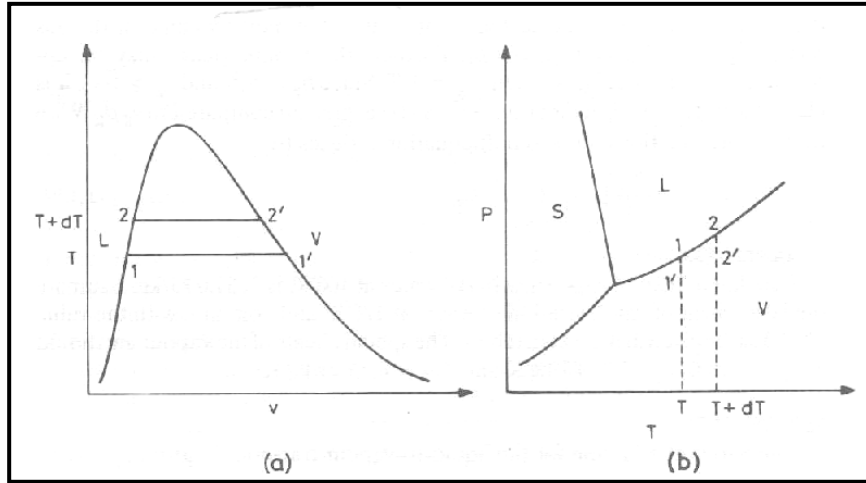
Consider the vaporization of a liquid at constant temperature and pressure as shown in figure.

The latent heat of vaporization associated with the phase change 1 to 1' is $(\hat{h}_{g1} - \hat{h}_{f1})$ at temperature T. When the saturation temperature is raised to (T+dT), the latent heat of vaporization is $(\hat{h}_{g2} - \hat{h}_{f2})$. The change in latent heat,

$$d \hat{h}_{fg} = d \hat{h}_g - d \hat{h}_f$$

The variation in the enthalpy associated with the variation in the independent variables T and

P is given by:



$$d\hat{h} = \hat{C}_p dT + \hat{v}(1 - \beta T)dP$$

or,

$$d\hat{h}_{fg} = (\hat{C}_{pg} - \hat{C}_{pf})dT + [(\hat{v}_g - \hat{v}_f) - (\hat{v}_g \beta_g - \hat{v}_f \beta_f)T]dP$$

$$\frac{\partial \hat{h}_{fg}}{\partial T} = (\hat{C}_{pg} - \hat{C}_{pf}) + [(\hat{v}_g - \hat{v}_f) - (\hat{v}_g \beta_g - \hat{v}_f \beta_f)T] \left(\frac{\partial P}{\partial T} \right)_{sat}$$

Substituting for $(dP/dT)_{sat}$ from the clapeyron equation,

$$\frac{\partial \hat{h}_{fg}}{\partial T} = (\hat{C}_{pg} - \hat{C}_{pf}) - \frac{(\hat{v}_g \beta_g - \hat{v}_f \beta_f) \hat{h}_{fg}}{(\hat{v}_g - \hat{v}_f)} + \frac{\hat{h}_{fg}}{T}$$

This is known as **Kirchoff relation**.

For a solid-to-liquid transition, it is a reasonably good approximation to assume that the molar heat capacity and the molar volume are constant in each phase and the coefficient of volume expansion β is negligible for each phase. Then,

$$\frac{\partial (\hat{h}_{sf}/T)}{\partial T} = \frac{\hat{C}_{pf} - \hat{C}_{ps}}{T} \text{ where } \hat{h}_{sf} \text{ is the latent heat of fusion.}$$

For the transition from liquid phase to vapour phase, the molar volume of the liquid phase can be neglected compared to the molar volume of the gas phase, and $\beta_g \gg \beta_f$. The vapour phase may be approximated as an ideal gas. Then $\beta_g = 1/T$. It is clear that $v_g \beta_g > v_f \beta_f$. Hence,

$$\frac{\partial \hat{h}_{fg}}{\partial T} = (\hat{C}_{pg} - \hat{C}_{pf})$$

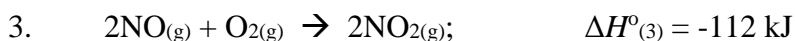
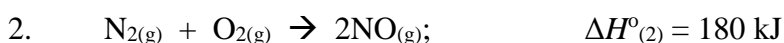
HESS'S LAW:

Since enthalpy is a state function, the change in enthalpy in going from some initial state to some final state is independent of the pathway. *Hess's law* states that *the change in enthalpy (ΔH) in going from a particular set of reactants to a particular set of products is the same regardless of the number of steps the reactions take.*

For example, when nitrogen gas is completely burned to NO_2 , $\Delta H^\circ = 68 \text{ kJ/mol}$ nitrogen.



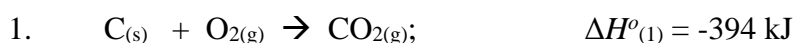
If nitrogen is converted to NO and the nitrogen monoxide is then converted to NO_2 , the total amount of heat absorbed is also equal to 68 kJ:



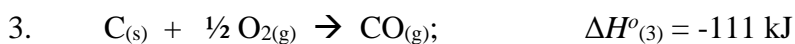
Thus, if reaction (1) + reaction (2) = reaction (3), then $\Delta H_{(1)} + \Delta H_{(2)} = \Delta H_{(3)}$; where $\Delta H_{(1)}$, $\Delta H_{(2)}$ and $\Delta H_{(3)}$ are enthalpy changes for reaction (1), reaction (2), and reaction (3), respectively.

According to the Hess's law, *if two or more reactions can be combined to produce an overall reaction, then the enthalpy of the overall reaction is equal to the sum of the enthalpy of individual reactions.*

Hess's law can be used to calculate the enthalpy of a particular reaction in a series of reactions for which the enthalpy of the net reaction and those of the other reactions in the series are known. Hess's Law is useful for calculating the enthalpy of reactions, which cannot be measured directly. For instance, the enthalpy of formation of carbon monoxide, CO, cannot be obtained experimentally because when carbon is burned in a limited oxygen supply, the product will always be a mixture of CO and CO₂. On the other hand, the enthalpy for the complete combustion of carbon to CO₂ and for the reaction to convert CO to CO₂ can be experimentally measured with a bomb-calorimeter. For example:



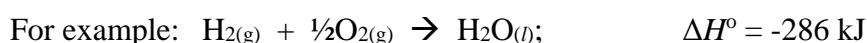
If we subtract equation (1) with equation (2), we obtain equation(3) and its enthalpy change:



$$\Delta H^{\circ}_{(3)} = \Delta H^{\circ}_{(1)} - \Delta H^{\circ}_{(2)} = -394 \text{ kJ} - (-283 \text{ kJ}) = -111 \text{ kJ}$$

Note that:

1. If the reaction is reverse, the sign of ΔH is also reversed (“+” \rightarrow “-“; “-“ \rightarrow “+”)
2. The magnitude of ΔH is directly proportional to the quantity of reactants and products. If the coefficients in a balanced equation are multiplied by an integer, the numerical value of ΔH is also multiplied by the same factor.
3. In a given reaction, the quantity of heat produced or absorbed is proportional to the molar amount of the limiting reactant.



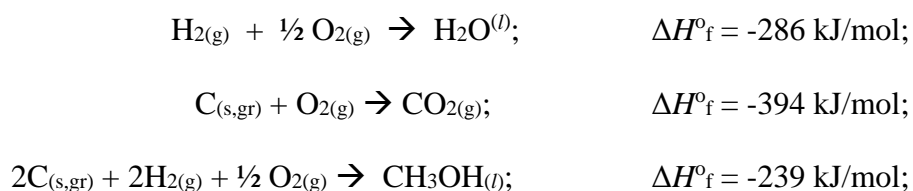


Standard Enthalpies of Formation

ΔH values are temperature and pressure dependent. It is necessary to specify both conditions when a table of enthalpy data is made. The *standard state* of an element or a compound is the form in which the substance is most stable under standard condition, which is 1 atm and 25 °C. For example, at 1 atm and 25 °C, the most stable form of oxygen is the gas containing diatomic molecules, O₂, and for carbon is the solid graphite.

When a reaction occurs with all reactants and products in their standard states under standard conditions, *the enthalpy change is known as the standard enthalpy change*, ΔH° , where the superscript “°” indicates standard conditions.

The *Standard enthalpy of formation* (ΔH°_f) is defined as *the change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard state in its standard state*. For example,



The following expression represents *Hess's law* that applies to the calculation of enthalpy of a reaction when the standard enthalpy of formations of various reactants and products are known.

$$\Delta H^\circ_{\text{rxn}} = \Delta [n_p \Delta H^\circ_f (\text{products})] - \Delta [n_r \Delta H^\circ_f (\text{reactants})]$$

The enthalpy of formation of all pure elements in their standard state is assigned zero value.

Enthalpy Changes of Ionic Reactions in Aqueous Solutions

In neutralization reaction: $\text{H}^+_{(aq)} + \text{OH}^-_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)}$; $\Delta H_n = -56 \text{ kJ/mol H}_2\text{O}$.

In solution under standard condition (i.e., 1 M solution and at 25°C), $\Delta H^{\circ}_f[\text{H}_3\text{O}^+(\text{aq})] = 0$;

Then $\Delta H^{\circ}_f[\text{OH}^-(\text{aq})]$ is calculated as follows:

$$\Delta H_f[\text{OH}^-(\text{aq})] = \Delta H_n - \Delta H_f[\text{H}_2\text{O}(l)] - \Delta H_f[\text{H}_3\text{O}^+(\text{aq})]$$

$$-56 \text{ kJ} = -286 \text{ kJ} - 0 - \Delta H_f[\text{OH}^-(\text{aq})]$$

$$\Delta H_f[\text{OH}^-(\text{aq})] = -286 \text{ kJ} - 0 + 56 \text{ kJ} = -230.0 \text{ kJ/mol}$$

THE SECOND AND THIRD LAWS OF THERMODYNAMICS

From experience we know that there are processes that satisfy the first law of thermodynamics (conservation of energy) yet never occur (*i.e. a stone that spontaneously jumps and cools, heat transferred from cold to hot body, chemical reaction diverting from its equilibrium state*).

the second law brings criteria for the direction of the **spontaneous** chemical or physical change of the thermodynamic system. Bear in mind, that generally the spontaneous processes are not reversible.

The historical roots of the second law stem from the invention of the heat engine (*namely, the steam engine*). It was known, that work can be fully converted to heat. The question is, what are the limitations on converting heat to work.

Historical statements of the second law

The Kelvin statement: There exists no thermodynamic transformation whose sole effect is to extract heat from a given reservoir and to convert it entirely into work.

The Clausius statement: There exists no thermodynamic transformation whose sole effect is to extract heat from a colder reservoir and to deliver it to a hotter reservoir.

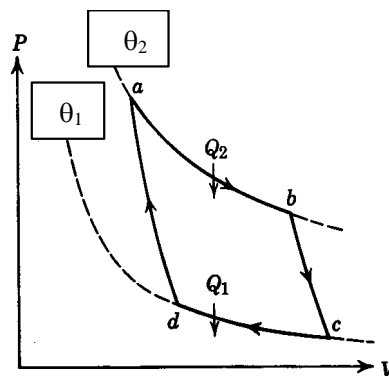
In both statements the key word is sole. It is possible to expand ideal gas isothermally and to convert entirely heat to work since $\Delta U=0$; However, the gas expands. Alternative statements of the second law address this problem by referring to a **cyclic process**.

We can prove that the above statements are equivalent, by showing that if one is false the other is false.

Carnot Heat Engine:

A *heat engine* generates mechanical works by carrying a “working substance” through a cyclic process.

The general Carnot heat engine is a reversible cyclic heat engine consisting of two adiabatic and two isothermal processes (*not necessarily in ideal gas*). operating between two experimental temperatures θ_1 and θ_2 . We choose to have $\theta_2 > \theta_1$. The cycle consists of the following trajectories:



1. ab - Isothermal expansion at θ_2 . Heat $|q_2|$ is absorbed by the system and $|w_{ab}|$ is performed by the system.
2. bc - adiabatic expansion from θ_2 to θ_1 $q = 0$ and w_{bc}
3. cd- isothermal compression at θ_1 q_1 and w_{cd}
4. da- adiabatic compression from θ_1 to θ_2 $q=0$ and w_{da}

In the above cyclic process $w = w_{ab} + w_{bc} + w_{cd} + w_{da}$

While $q = q_1 + q_2 = (q_{ab} + q_{cd})$.

According to the first law $\Delta U = 0$; namely $w = -(q_1 + q_2)$

Since usually we extract heat from the hot reservoir at θ_2 , the efficiency of the Carnot cycle is defined as :

$$\eta \equiv -w/q_2 = (q_1 + q_2)/q_2 = 1 + q_1/q_2 .$$

Since q_1 and q_2 are of opposite signs (we will prove soon) the efficiency is smaller than 1.

Note that the cycle can be complex. i.e. composed of two materials A and B each having its own equation of state: $f_A(p_A, V_A, \theta) = 0$; and $f_B(p_B, V_B, \theta) = 0$; It is imperative however that they operate between θ_1 and θ_2 . We shall now show some important formal consequences of the second law of thermodynamics.

A. q_1 and q_2 are of opposite signs:

Suppose that the q_1 and q_2 are not of opposite signs. Then, we can choose the direction of a Carnot cycle so that $w = -(q_1 + q_2) < 0$; We can then convert portion of the work $|q_1|$ to heat at the reservoir at θ_1 so that the net result of the whole process will be conversion of q_2 to work in contradiction to the Kelvin statement. Conclusions: q_1 and q_2 are of opposite signs.

B. The ratio of q_1 and q_2 depends on θ_1 and θ_2 only.

Let us couple two Carnot engines working between two identical temperatures θ_1 and θ_2 ($\theta_2 > \theta_1$). For the first engine $w = -(q_1 + q_2)$; For the second engine $w' = -(q_1' + q_2')$. Let us find integers so that $n|q_1| = m|q_1'|$. We will choose the direction of the engines so that q_1 and q_1' have opposing signs so that $nq_1 + mq_1' = 0$; The net result of this choice is that no heat is absorbed in the cold reservoir held at θ_1 . According to the first law:

$$\Delta U = 0 \Rightarrow w = -(nq_2 + mq_2') - (nq_1 + mq_1')$$

In order not to violate the second law according to Kelvin $w > 0$ (*Work can be done on the system and converted to heat*). Therefore: $nq_2 + mq_2' \leq 0$;

But since we can run the whole cycle backward we can prove that: $-(nq_2 + mq_2') \leq 0$;

The conclusion is that only the equality sign is general: $nq_2 + mq_2' = 0$;

Yet, we have chosen: $nq_1 + mq_1' = 0$;

Hence by dividing the last two expressions: $-q_1/q_2 = -q_1'/q_2'$

We may therefore infer the existence of a **universal** function having the property that:

For any Carnot cycle $-q_1/q_2 = f(\theta_1, \theta_2)$

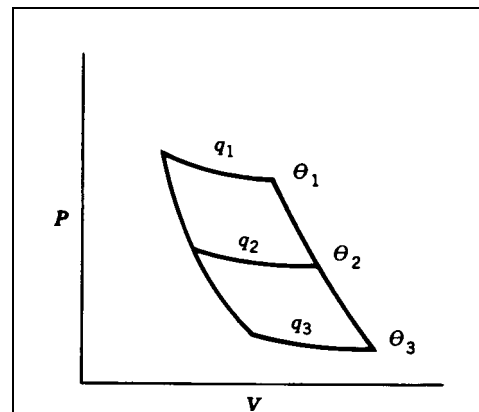
C. The Thermodynamic scale of temperature:

Let us examine three general Carnot cycles:

$$-q_1/q_2 = f(\theta_1, \theta_2)$$

$$-(-q_2)/q_3 = f(\theta_2, \theta_3)$$

$$-q_1/q_3 = f(\theta_1, \theta_3)$$



By multiplying the first two expressions and comparing the result with the third expression one gets:

$$f(\theta_1, \theta_3) = f(\theta_1, \theta_2) f(\theta_2, \theta_3).$$

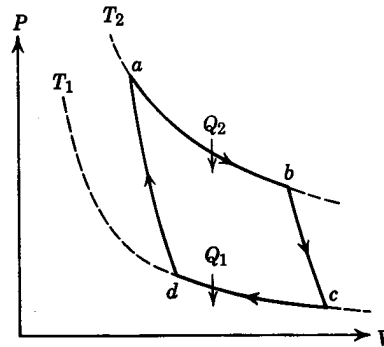
Since the LHS does not depend on θ_2 The RHS does not depend either and $f(\theta_1, \theta_2)$ must take the form of :

$$f(\theta_1, \theta_2) = g(\theta_1) / g(\theta_2)$$

We have just defined a **universal Thermodynamic temperature scale**. $T_{\text{thermodynamic}} = g(\theta)$.

D. The relation between the thermodynamic and the experimental ideal-gas temperature scales:

By applying a Carnot cycle to ideal-gas as in the figure, one can relate the experimental and the thermodynamic temperature scales. For the cycle:



$$w = -nRT_2 \ln \frac{V_b}{V_a} + \int_{T_2}^{T_1} C_v dT - nRT_1 \ln \frac{V_d}{V_c} + \int_{T_1}^{T_2} C_v dT$$

The second and the fourth terms cancel. By using the relations for adiabatic expansion of ideal gases:

$$T_2 V_b^{\gamma-1} = T_1 V_c^{\gamma-1} \quad \text{and} \quad T_2 V_a^{\gamma-1} = T_1 V_d^{\gamma-1} \quad (T_a = T_b = T_2; \quad T_c = T_d = T_1)$$

we obtain $V_b/V_a = V_c/V_d$. Substituting this relation into the work expression results in: $w = -nR(T_2 - T_1) \ln V_b/V_a$.

$q_2 = -w_{ab} = nRT_2 \ln V_b/V_a$ and $q_1 = -w_{cd} = nRT_1 \ln V_d/V_c$ since $\Delta U = 0$ for isothermal process of ideal gas.

From volume relations q_1 also equals: $-nRT_1 \ln V_b/V_a \quad \Rightarrow \quad -q_1/q_2 = T_1/T_2$

Since $-q_1/q_2 = f(\theta_1, \theta_2) = g(\theta_1)/g(\theta_2)$ and for ideal gas $-q_1/q_2 = T_1/T_2$ and since $g(\theta)$ is universal: the thermodynamic temperature scale is proportional to the ideal-gas temperature scale.

Entropy and Clausius theorem:

We have obtained that for the Carnot cycle (a cyclic and reversible process) $-q_1/q_2 = T_1/T_2$.

A rearrangement of the terms leads to:

$q_1/T_1 + q_2/T_2 = 0$: One can generalize this conclusion to any combination of Carnot cycles:

The Clausius Theorem: In any cyclic process throughout which the temperature is defined the following inequality holds: $\int dq/T \leq 0$; where the equality holds for a reversible process.

proof: Let the cyclic transformation divided into n infinitesimal steps. The system is imagined to be brought successively into thermal contact with heat reservoirs at temperature T_i and heat q_i is absorbed from it by the system. the theorem is obtained by letting $n \rightarrow \infty$. Consider also n Carnot cycles. For the i -th cycle C_i

1. Absorb q_i^0 from T_0
2. Operate between T_i and T_0 (where $T_0 \geq T_i$ for all i)
3. Reject amount of q_i to T_i

We have shown that $-q_i^0/q_i = T_0/T_i$.

Consider combination of the cyclic process and $\{C_i\}$. The net result of this cycle is that the amount of heat $Q_0 \equiv \sum q_i^0 = -T_0 \sum (q_i/T_i)$ is absorbed from the reservoir at T_0 by the system and converted entirely into work without other effect. According to Kelvin (second law) $Q_0 \leq 0$; Therefore:

$$\sum (q_i/T_i) \leq 0; \Rightarrow \int dq/T \leq 0; \text{ (the signs for the Carnot cycles and the system are opposite)}$$

If the process is reversible we can reverse its direction. $\sum (q_i/T_i) \geq 0$

We can deduce that for the reversible process the equality holds: $\sum q_i/T_i = 0 \Rightarrow \int dq/T = 0$;

We have defined a new state function whose differential form is $dS = dq_{rev}/T$. Although heat by itself is not a state function. This new state function is defined as Entropy S :

Entropy changes in reversible and irreversible processes

The practical implications of the entropy function rest on the manipulation of the above expression. Since the cyclic integration of dS equals zero the difference between S values of two states does not depend on the path.

For irreversible processes between two states A and B we can compose a cyclic process between A and B, which is irreversible in **original path and direction** and reversible (any reversible path) on the other direction.

$$\int_{\text{cyclic}} dq/T = \int_A^B dq_{\text{irrev}}/T + \int_B^A dq_{\text{rev}}/T = \int_A^B dq_{\text{irrev}}/T - \Delta S_{AB} \leq 0;$$

The conclusion is that:

$$\text{For every irreversible process: } \Delta S_{AB} \geq \int_{AB} dq_{\text{irrev}}/T$$

For an isolated system $q_{\text{irrev}} = 0$. $\Delta S_{AB} \geq 0$ (irreversible process) or $\Delta S_{AB} = 0$ (the reversible process)

For an isolated system, the *spontaneous* transition from one equilibrium state to another is triggered by removal of constraints (*i.e. sudden thermal contacts between its parts.*) and the entropy increases

Thermal efficiency of heat engines:

We have shown that for the Carnot heat engine the efficiency is defined as:

$$\eta \equiv -w/q_2 = (q_1 + q_2)/q_2 = 1 + q_1/q_2 \Rightarrow \eta = 1 - T_1/T_2 \quad (T_2 > T_1). \text{ We will prove now the } \mathbf{Carnot}$$

theorem:

No engine operating between two given temperature is more efficient than a Carnot engine.

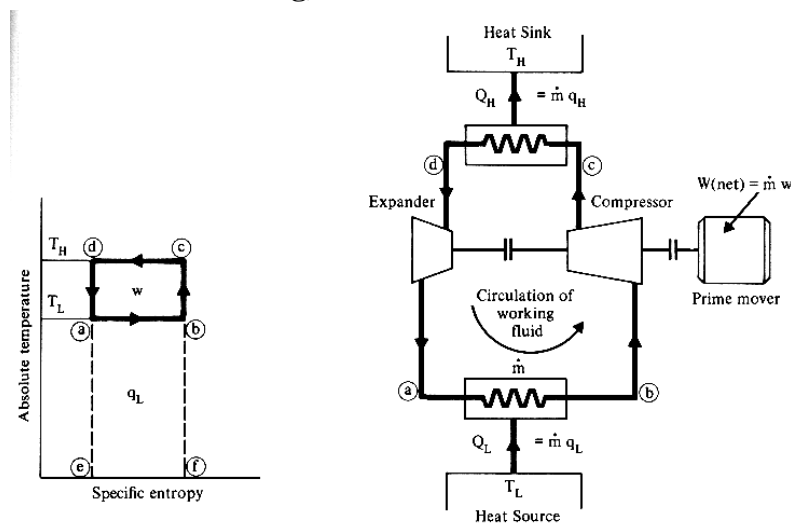
$\eta = 1 + q_1/q_2$. Let us assume a "more efficient" engine with $\eta' = 1 + q_1'/q_2'$. if $\eta' > \eta$ then:

$1 + q_1'/q_2' > 1 + q_1/q_2$. Let us scale the machines so that $q_1 = q_1'$ in the direction where both engine serve as heat machines. $\Rightarrow q_2' < q_2$ since q_1 is negative. Now we reverse the "efficient"

engine and operate both engines: $q_{\text{total}} = q_2' - q_2 < 0$ which was converted completely to work, in contradiction to the Kelvin statement of the 2nd law.

Remarks about the efficiency of refrigeration and heat-pump cycles:

Consider the Carno cycle described below which is operated in a reversed direction to the Carno heat engine. Work is done on the system ($w > 0$) while heat is absorbed by the system at the cold junction (T_L) (**can be used as refrigerator**) and dissipated by the system at the hot junction (T_H) (**Can be used for heating**).



Let us consider the efficiencies of these processes:

η (cooling) = q_L / w since we are interested in the ratio between the heat absorbed (q_L) and the work done on the Carno engine. η (cooling) = $q_L / -(q_L + q_H) = -1 / (1 - T_H/T_L) = T_L / (T_H - T_L)$

η (heating) = $-q_H / w$ since we are interested in the ratio between the heat dissipated ($-q_H$) and the work done on the Carno engine. η (heating) = $-q_H / -(q_L + q_H) = 1 / (1 - T_L/T_H) = T_H / (T_H - T_L)$

Note that cooling efficiencies may be larger than 1. This is consistent with energy conservation since heat is transferred by the work and not generated. Note that the efficiency

of the ideal "heat-pump" is always larger than 1, since in addition to the heat transferred the work has been converted to heat.

Examples for entropy changes:

Isothermal expansion of ideal gas.

In the ideal gas $\Delta U = 0$ for isothermal expansion. Therefore dq equals $-\delta w$.

$$\Delta S = \int dq_{\text{rev}}/T = \int pdV/T = \int nR dV/V = nR \ln (V_2/V_1).$$

Adiabatic free expansion of ideal gas. (NO work is done)

The Joule experiment has shown that no temperature change occurs on free expansion of ideal gas. Therefore although this is an irreversible process ΔS can be calculated as before, since the initial and final states are equal. $\Delta S = nR \ln (V_2/V_1)$. Note that in both processes also $\Delta U = 0$.

The difference between the two processes is that in the isothermal expansion both dq and $\delta w \neq 0$.

General expansion of ideal gas:

For any initial and final state of the ideal gas it is convenient to divide the expansion path to two paths i.e. isothermal and isochoric:

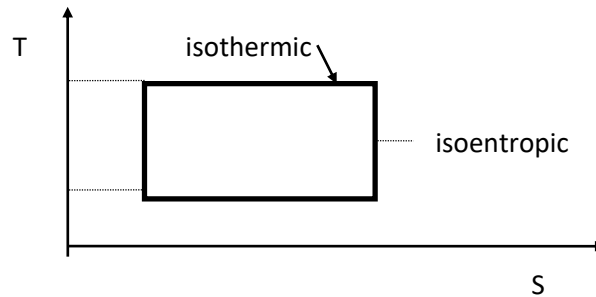
$\Delta S = \int C_v dT/T + \int pdV/T = C_v \ln (T_2/T_1) + nR \ln (V_2/V_1)$. This expression is valid for any process in the ideal gas in which the initial (T_1, V_1) and final (T_2, V_2) states are known, and under the assumption that in the relevant range C_v is constant.

$$\Delta S_{\text{ideal}} = C_v \ln (T_2/T_1) + nR \ln (V_2/V_1).$$

it can be easily shown that in analogy $\Delta S_{\text{ideal}} = C_p \ln (T_2/T_1) - nR \ln (P_2/P_1)$ for $(T_1, p_1) \rightarrow (T_2, p_2)$.

Adiabatic reversible expansion.

Since $dq_{rev} = 0$ in any step of this expansion $\Delta S = 0$. Adiabatic reversible expansion is also called isentropic expansion. The Carnot cycle is thus represented in T-S coordinates as a square.



Adiabatic irreversible expansion:

Again we refer to expansion between V_1 and V_2 . We assume that V_2 so that the 2 Kg weight will stop at V_2 .

$$w = -p_{ext}(V_2 - V_1), \quad q = 0 \Rightarrow \Delta U = -p_{ext}(V_2 - V_1) = \int C_v dT \Rightarrow \Delta T = -p_{ext}(V_2 - V_1)/C_v$$

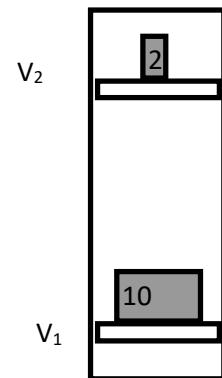
$$\text{also } P_1 V_1 / T_1 = P_2 V_2 / T_2, \quad P_2 = 0.2 P_1 \Rightarrow T_2 = 0.2 V_2 T_1 / V_1$$

Let us assume that $n=1$, $P_1=1 \text{ atm}$, $T_1=273 \Rightarrow V_1 = 22.4 \text{ l}$ $C_v=1.5 R$

$$0.082 = 0.2 V_2 / T_2 \quad V_2 / T_2 = 0.41 \quad V_2 / 0.41 - 273 = -0.2(V_2 - 22.4) / 0.123$$

$$2.43 V_2 - 273 = -1.63 V_2 + 36.5 \quad V_2 = 310 / 3.06 = 101.3 \text{ l} \quad T_2 = 247 \text{ }^\circ\text{K}$$

$$\Delta S_{ideal} = (1.5 \ln(247/273) + \ln(101/22.4)) * 8.314 = 11.2 \text{ J}^\circ\text{K}^{-1}$$



For the reverse process again $\Delta T = -p_{ext}(V_2 - V_1)/C_v$ and $P_1 V_1 / T_1 = P_2 V_2 / T_2$

$$\text{This time } V_2 / T_2 = 0.082 \quad V_2 / 0.082 - 247 = -1(V_2 - 101.3) / 0.123$$

$$20.32 V_2 = 1070 \quad V_2 = 52.7 \text{ l} \quad T_2 = 643 \text{ }^\circ\text{K}$$

$$\Delta S_{ideal} = (1.5 \ln(643/247) + \ln(52.7/101.3)) * 8.314 = 6.5 \text{ J}^\circ\text{K}^{-1}$$

The calorimetric determination of entropies:

For any substance entropy change from 0°K can be evaluated by integrating dq_{rev}/T

$$S_T - S_0 = \int_0^{T_m} C_p(s) / T + \Delta H_{fus} / T_m + \int_{T_m}^{T_b} C_p(l) / T + \Delta H_{vap} / T_b + \int_{T_b}^T C_p(g) / T$$

One can refer to isobaric or isochoric processes. C_p would be replaced by C_v for isochoric processes.

(*somewhat cumbersome for gas and solid together*). The same procedure can be used to evaluate entropy changes of substances between two temperatures.

The fundamental equation for a closed system:

The first and the second laws of thermodynamics can be combined for a **closed system** (*of constant composition*). Since U is a state function the differential dU in any process can be obtained from a reversible process having the same change in state: For a reversible process $\delta q = TdS$ and $\delta w = -pdV$ for a pressure volume work so that:

$$dU = TdS - p dV$$

(*This equation is called the **fundamental equation** for a closed system*)

It is always valid of course, also for irreversible processes where $\delta q < TdS$ and $\delta w > -pdV$

$$\text{Since } dU = (\partial U / \partial S)_V dS + (\partial U / \partial V)_S dV \Rightarrow T = (\partial U / \partial S)_V \text{ and } p = -(\partial U / \partial V)_S$$

This equation can be rewritten as:

$dS = dU/T + p/T dV$ indicating that increase in the internal energy at constant volume or increase in the volume at constant energy will increase entropy.

Entropy of mixing

To calculate the change of entropy when a partition is withdrawn between two volumes (V_1 and V_2) of ideal **different** gases we recall that ideal gases do not interact and therefore we can consider a situation in which each gas is expanded into the total volume $V = V_1 + V_2$.

$$\Delta S = n_1 R \ln (V/V_1) + n_2 R \ln (V/V_2)$$

In the case of **identical** gases of equal pressure, the removal of the partition practically does not change the state of the system, and the formal change of entropy $(n_1 + n_2) R \ln 2$ is not valid. This paradox is known as the **Gibbs paradox**, and is resolved by demanding that for the purposes of entropy changes the gases should be distinguishable.

THIRD LAW OF THERMODYNAMICS:

So far we referred to entropy changes only. Early in this century, it was found by Richards and by Nernst, that, according to experience for any process: $\lim_{T \rightarrow 0} \Delta S(T) = 0$; This has led Nernst to formulate the third law of thermodynamics which casts absolute values to entropy:

The entropy of each pure element or substance at perfect crystalline form is zero at absolute zero

Experimentally there are violations which result from imperfect crystalline forms at very low temperatures. Isotope disorder and spin degeneracy are ignored in chemistry since they are the same in the reactants and products.

There are two experimental implications to the third law:

1. C_V at low temperatures. Since $S(T) = \int C_V/T \, dT + \dots$ to make the contribution of low temperatures infinitesimally small $C_V(T)_{T \rightarrow 0} \sim T^{1+\gamma}$ where $\gamma > 0$.

2. The absolute zero cannot be reached in infinite number of steps. This is an alternative statement of the third law.

The third law is consistent with the microscopic picture since at the absolute zero the perfect crystal is always in the ground state and the number of probable states is one (*practically zero*).

Entropy changes for chemical reactions:

The standard reaction entropy $\Delta_r S^0$ for a reaction $\sum \nu_i A_i = 0$ is equal to the change in entropy when the separated reactants, each in its standard state are converted to the separated products each in its standard state. $\Delta_r S^0 = \sum \nu_i \underline{S}_i^0$ where \underline{S}_i^0 are the molar entropies at the standard conditions.

To calculate the standard entropy of reaction for another temperature:

$$\Delta_r S^0(T) = \Delta_r S^0(298) + \int \Delta C_p^0/T dT$$

GIBBS ENERGY AND HELMHOLTZ ENERGY

Typical Thermodynamic functions:

We have expressed dS in terms of a differential of state function $dU = TdS - pdV$ in terms of the intensive T and p and the extensive S and V . The pairs T - S and p - V are called *conjugate variables*, where S and V serve the role of the independent variables which can be changed at will. It is not always practical or desirable to use these variables as independent, and we wish to change them. We can express $U(T, V)$ but then we lose the information of the second law. The Legendre Transform gives us the appropriate tools.

The Legendre transform:

If a function $Z(z_1, z_2, \dots)$ has the natural variables z_1, z_2, \dots , its differential is of the form:

$$dZ = Z_1 dz_1 + Z_2 dz_2 + \dots = (\partial Z / \partial z_1) dz_1 + (\partial Z / \partial z_2) dz_2 + \dots$$

To develop a Legendre transform Y of Z that has Z₁ as independent variable we define Y as:

$$Y = Z - z_1 Z_1$$

The differential of the extensive function Y is:

$$dY = dZ - z_1 dZ_1 - Z_1 dz_1 = -z_1 dZ_1 + Z_2 dz_2 + \dots$$

We have generated a differential of a new function where the role of the extensive and intensive variables has changed as well as the sign.

We have already recognized one example.

$$dU = TdS - pdV \quad \text{we wish to replace the roles of p and V} \Rightarrow$$

$$H = U + pV \quad (\text{enthalpy})$$

$$dH = dU + d(pV) = \delta q - pdV + (pdV + Vdp) = \delta q + Vdp = TdS + Vdp$$

in a similar way when we wish to transfer to T and V as independent variables we get the

Helmholtz free energy function:

$$A = U - (\partial U / \partial S)_V S = U - TS$$

$$dA = TdS - pdV - TdS - SdT = -SdT - pdV$$

When we wish to transfer to p and T as independent variables we get the ***Gibbs free energy***

$$G = U - (\partial U / \partial V)_S V - (\partial U / \partial S)_V S = U + pV - TS = H - TS$$

$$dG = -SdT + Vdp$$

All the above relations are not restricted to one component systems. They are restricted to material exchange with the surrounding. All the above new generated functions are **state functions** since they are superposition of state functions and state variables.

Thermodynamic derivatives for closed systems

Since dU dH dA dG are exact differentials (of state functions) the following derivatives can be deduced.

$dU=TdS-pdV$	$\Rightarrow (\partial U/\partial S)_V = T$	$(\partial U/\partial V)_S = -p$
$dH=TdS+Vdp$	$\Rightarrow (\partial H/\partial S)_p = T$	$(\partial H/\partial p)_S = V$
$dA=-SdT-pdV$	$\Rightarrow (\partial A/\partial T)_V = -S$	$(\partial A/\partial V)_T = -p$
$dG=-SdT+Vdp$	$\Rightarrow (\partial G/\partial T)_p = -S$	$(\partial G/\partial p)_T = V$

Now, we are in a position to illustrate that if a thermodynamic potential is known as a function of its natural variable (i.e. T and p for G) we can calculate all the thermodynamic properties of the system. $S=-(\partial G/\partial T)_p$ $V=(\partial G/\partial p)_T$ $U = G - PV + TS = G - p(\partial G/\partial p)_T - T(\partial G/\partial T)_p$

$$A = G - p(\partial G/\partial p)_T \quad H = G - T(\partial G/\partial T)_p$$

MAXWELL RELATIONS:

Since dU dH dA and dG are exact differentials the mixed second derivatives of the coefficients of the two terms are equal. This yields the following Maxwell relations:

$dU=TdS-pdV$	$(\partial T/\partial V)_S = -(\partial p/\partial S)_V$	I
$dH=TdS+Vdp$	$(\partial T/\partial p)_S = (\partial V/\partial S)_p$	II
$dA=-SdT-pdV$	$(\partial S/\partial V)_T = (\partial p/\partial T)_V$	III
$dG=-SdT+Vdp$	$-(\partial S/\partial p)_T = (\partial V/\partial T)_p$	IV

These relations are important because they enable us to express any thermodynamic property in terms of easily measured physical properties. We will demonstrate this issue in few examples:

The dependence of entropy on state variables:

$$dS = (\partial S / \partial T)_p dT + (\partial S / \partial p)_T dp = C_p/T dT - (\partial V / \partial T)_p dp = C_p/T dT - \alpha V dp \quad (\text{using relation IV})$$

$$dS = (\partial S / \partial T)_V dT + (\partial S / \partial V)_T dV = C_V/T dT + (\partial p / \partial T)_V dV = C_V/T dT + \alpha/\beta dV \quad (\text{using relation III})$$

where α and β are the volume expansion coefficient and compressibility respectively.

Note that we have used Maxwell relation to relate entropy derivatives to equation of state derivatives. Note that we use the following relation to evaluate $(\partial p / \partial T)_V$: $(\partial p / \partial T)_V = -(\partial V / \partial T)_p / (\partial V / \partial p)_T = \alpha/\beta$

Thermodynamic equation of state:

by using $dU = TdS - pdV$ we derive that at constant temperature:

$$(\partial U / \partial V)_T = T (\partial S / \partial V)_T - p$$

Using Maxwell relation III we deduce:

$$(\partial U / \partial V)_T = T (\partial p / \partial T)_V - p = \alpha/\beta T - p$$

This relation is often called internal pressure. It has dimensions of pressure and is due to molecular attraction and repulsion (*equals zero for ideal gases*).

$C_p - C_v$:

As we have already shown:

$$C_p - C_v = [p + (\partial U / \partial V)_T] \alpha V$$

Now by using the expression of the previous paragraph:

$$C_p - C_V = [p + \alpha/\beta T - p] \alpha V = \alpha^2/\beta VT \quad (\text{for ideal gases } = nR)$$

Effect of temperature on the Gibbs energy:

Since $(\partial G/\partial T)_p = -S$ and S is always positive G decreases with the temperature for constant pressure. Recall that $G = H - TS \Rightarrow G = H + T(\partial G/\partial T)_p$

$$(\partial(G/T)/\partial T)_p = -G/T^2 + 1/T (\partial G/\partial T)_p \quad \text{By using the previous expression:}$$

$$(\partial(G/T)/\partial T)_p = -H/T^2$$

$$\text{But } (\partial(G/T)/\partial T^{-1})_p = (\partial(G/T)/\partial T)_p * (\partial T/\partial T^{-1}) = H$$

This relation can be expanded for Gibbs energy changes:

$(\partial(\Delta G/T)/\partial T)_p = -\Delta H/T^2$ and $(\partial(\Delta G/T)/\partial T^{-1})_p = \Delta H$ This is the Gibbs Helmholtz relation and is useful for the evaluation of free energy changes from measurements of ΔH

Effect of pressure on the Gibbs energy:

$$\text{For constant } T \quad \text{since } (\partial G/\partial p)_T = V \quad dG = V dp \Rightarrow \Delta G = \int V dp$$

For solids or liquids V is practically independent of pressure $\Rightarrow \Delta G = V \Delta P$

For ideal gas the integration becomes $\Delta G = nRT \int dp/p = nRT \ln(p_2/p_1)$

It is practical to define reference conditions of pressure p_0 (and temperature) which lead to:

$$G(p) = G^0 + nRT \ln(p/p_0)$$

CLAUSIUS-CLAPEYRON EQUATION:

To find out the dependence of pressure on equilibrium temperature when two phases coexist.

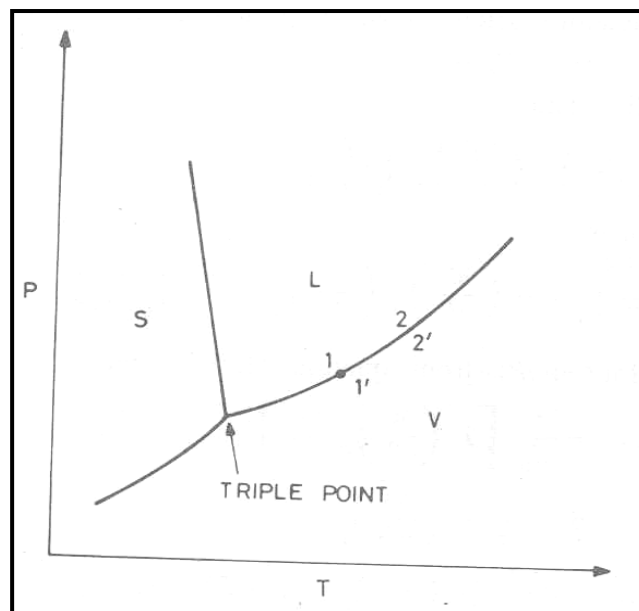
Along a phase transition line, the pressure and temperature are not independent of each other, since the system is univariant, that is, only one intensive parameter can be varied independently.

When the system is in a state of equilibrium, i.e., thermal, mechanical and chemical equilibrium, the temperature of the two phases has to be identical, the pressure of the two phases has to be equal and the chemical potential also should be the same in both the phases.

Representing in terms of Gibbs free energy, the criterion of equilibrium is:

$$d\hat{g} = 0 \text{ at constant } T \text{ and } P$$

$$\text{or, } d\hat{g} = -\hat{s}dT + \hat{v}dP = 0$$



Consider a system consisting of a liquid phase at state 1 and a vapour phase at state 1' in a state of equilibrium. Let the temperature of the system is changed from T_1 to T_2 along the vaporization curve.

For the phase transition for 1 to 1':

$$d\hat{g} = -\hat{s}dT + \hat{v}dP = 0$$

$$\text{or } \hat{g}_{\text{liquidphase}} = \hat{g}_{\text{vaporphase}}$$

$$\text{or } \hat{g}_1 = \hat{g}_2$$

In reaching state 2 from state 1, the change in the Gibbs free energy of the liquid phase is given by:

$$\hat{g}_2 - \hat{g}_1 = -\hat{s}_f dT + \hat{v}_f dP$$

Similarly, the change in the Gibbs free energy of the vapour phase in reaching the state 2' from state 1' is given by:

$$\hat{g}_{2'} - \hat{g}_{1'} = -\hat{s}_g dT + \hat{v}_g dP$$

Therefore, $-\hat{s}_f dT + \hat{v}_f dP = -\hat{s}_g dT + \hat{v}_g dP$

$$\text{Or } \left(\frac{\partial P}{\partial T} \right)_{\text{sat}} = \frac{\hat{s}_g - \hat{s}_f}{\hat{v}_g - \hat{v}_f}$$

Where the subscript *sat* implies that the derivative is along the saturation curve.

The entropy change associated with the phase transition:

$$\hat{s}_g - \hat{s}_f = \frac{\hat{h}_g - \hat{h}_f}{T} = \frac{\hat{h}_{fg}}{T}$$

$$\text{Hence, } \left(\frac{\partial P}{\partial T} \right)_{sat} = \frac{\hat{h}_{fg}}{T \hat{v}_{fg}} = \frac{\Delta \hat{h}}{T \Delta \hat{v}}$$

Which is known as the **Clapeyron equation**

Since $\Delta \hat{h}$ is always positive during the phase transition, $\left(\frac{\partial P}{\partial T} \right)_{sat}$ will be positive or negative

depending upon whether the transition is accompanied by expansion ($\Delta \hat{v} > 0$) or contraction ($\Delta \hat{v} < 0$).

Consider the liquid-vapour phase transition at low pressures. The vapour phase may be approximated as an ideal gas. The volume of the liquid phase is negligible compared to the

volume of the vapour phase ($\hat{v}_g \gg \hat{v}_f$) and hence $\hat{v}_{fg} = \Delta \hat{v} = \hat{v}_g = RT/P$.

The Clapeyron equation becomes:

$$\left(\frac{\partial P}{\partial T} \right)_{sat} = \frac{\hat{h}_{fg} P}{RT^2}$$

$$\text{or } \frac{d \ln P}{dT} = \frac{\hat{h}_{fg}}{RT^2}$$

which is known as the **Clausius-Clapeyron equation**.

Assume that \hat{h}_{fg} is constant over a small temperature range, the above equation can be integrated to get,

$$\ln \frac{P_2}{P_1} = \frac{\hat{h}_{fg}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\text{or } \ln P = -\frac{\hat{h}_{fg}}{RT} + \text{constant}$$

Hence, a plot of $\ln P$ versus $1/T$ yields a straight line the slope of which is equal to $-(h_{fg}/R)$.

THE GIBBS-HELMHOLTZ EQUATION:

Derivation of the Gibbs-Helmholtz Equation

The Gibbs-Helmholtz equation provides information about the temperature dependence of the Gibbs free energy.

The derivation of the Gibbs-Helmholtz equation begins with the fundamental equation for the Gibbs free energy G ,

$$dG = -SdT + VdP$$

Using the relationships for an exact differential, we have that

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

Substituting this result for $-S$ into the equation defining the Gibbs free energy, $G = H - TS$, yields

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P$$

$$\frac{G}{T} = \frac{H}{T} + \left(\frac{\partial G}{\partial T}\right)_P$$

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = -\frac{G}{T^2} + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P$$

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = \frac{1}{T}\left[-\frac{G}{T} + \left(\frac{\partial G}{\partial T}\right)_P\right]$$

$$\begin{aligned} \left(\frac{\partial(G/T)}{\partial T}\right)_P &= \frac{1}{T} \left[-\frac{G}{T} + \left(\frac{\partial G}{\partial T}\right)_P \right] \\ &= \frac{1}{T} \left\{ -\left[\frac{H}{T} + \left(\frac{\partial G}{\partial T}\right)_P\right] + \left(\frac{\partial G}{\partial T}\right)_P \right\} \\ \left(\frac{\partial(G/T)}{\partial T}\right)_P &= -\frac{H}{T^2} . \end{aligned}$$

This provides one form of the Gibbs-Helmholtz equation.

Another useful form of the Gibbs-Helmholtz equation may be obtained by considering the derivative

$$\left(\frac{\partial(G/T)}{\partial(1/T)}\right)_P = -T^2 \left(\frac{\partial(G/T)}{\partial T}\right)_P$$

$$\left(\frac{\partial(G/T)}{\partial(1/T)}\right)_P = H$$

$$\boxed{\left(\frac{\partial(\Delta G/T)}{\partial(1/T)}\right)_P = \Delta H .}$$

Exploring the Temperature Dependence of the Gibbs Free Energy Change

For an endothermic and exothermic reaction, the slope of the Gibbs-Helmholtz equation is positive and negative, respectively.

