b) Applications of Thermodynamics – I (25 Lectures)

Partial properties and Chemical potential: Chemical potential and activity, partial molar quantities, relation between Chemical potential and Gibb's free energy and other thermodynamic state functions; variation of Chemical potential (μ) with temperature and pressure; Gibbs-Duhem equation; fugacity and fugacity coefficient; Variation of thermodynamic functions for systems with variable composition; Equations of states for these systems, Change in G, S H and V during mixing for binary solutions

Chemical Equilibrium: Thermodynamic conditions for equilibrium, degree of advancement; van't Hoff's reaction isotherm (deduction from chemical potential); Variation of free energy with degree of advancement; Equilibrium constant and standard Gibbs free energy change; Definitions of K_P, K_C and K_X; van't Hoff's reaction isobar and isochore from different standard states; Shifting of equilibrium due to change in external parameters e.g. temperature and pressure; variation of equilibrium constant with addition to inert gas; Le Chatelier's principle and its derivation

Nernst's distribution law; Application- (finding out K_{eq} using Nernst dist law for $KI+I_2 = KI_3$ and dimerization of benzene

Chemical potential and other properties of ideal substances- pure and mixtures: a) Pure ideal gas-its Chemical potential and other thermodynamic functions and their changes during a change of; Thermodynamic parameters of mixing; Chemical potential of an ideal gas in an ideal gas mixture; Concept of standard states and choice of standard states of ideal gases

b) Condensed Phase – Chemical potential of pure solid and pure liquids, Ideal solution – Definition, Raoult's law; Mixing properties of ideal solutions, chemical potential of a component in an ideal solution; Choice of standard states of solids and liquids

Conductance and transport number: Ion conductance; Conductance and measurement of conductance, cell constant, specific conductance and molar conductance; Variation of specific and equivalent conductance with dilution for strong and weak electrolytes; Kohlrausch's law of independent migration of ions; Equivalent and molar conductance at infinite dilution and their determination for strong and weak electrolytes; Debye –Huckel theory of Ion atmosphere (qualitative)-asymmetric effect, relaxation effect and electrophoretic effect; Ostwald's dilution law; Ionic mobility; Application of conductance measurement (determination of solubility product and ionic product of water); Conductometric titrations

Transport number, Principles of Hittorf's and Moving-boundary method; Wien effect, Debye-Falkenhagen effect, Walden's rule

THERMODYNAMICS OF OPEN SYSTEMS

CLASS-1

- Many equations we have learnt so far can be applied only to closed systems of constant composition.

- This limitation simply means that we have been dealing with a special case.

- To fix the state of a system, the values of two independent variables and the mole numbers of the components must be fixed.

- We have been able to neglect the mole numbers of the components so far because we have studied only closed systems of fixed composition.

- Now we will extend our discussion to the more general systems where the system’s composition is free to change.

For a closed system of fixed composition, the extensive thermodynamic properties such as V, U, S, A, and G are functions of any pair of convenient independent variables.

For example:

$$dG = VdP - SdT$$

suggests that G is a natural function of T and P. That is $G = f(T, P)$. The total differential of G would be

$$\begin{aligned} dG &= \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \\ &= -S(T, P)dT + V(T, P)dP \end{aligned}$$

When the composition of a system varies, the mole numbers of the components are additional independent variables and we have

$$G = f(T, P, n_1, n_2, \ldots, n_i, \ldots)$$

$$G = f(T, P, n_1, n_2, \ldots, n_i, \ldots)$$

Therefore, the total differential of G becomes

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \sum_{\substack{\text{all} \\ \text{components}}} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} dn_i$$

The partial derivative $(\partial G/\partial n_i)_{T,P,n_j}$, in which $i \neq j$, represents the rate of increase in the Gibbs function of the system per mole of component i added to the system when T, P, and the other mole numbers are held constant.

The summation is over all components of the system.

If the composition is constant, so that the dn_i terms are all zero,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \sum_{\substack{\text{all} \\ \text{components}}} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} dn_i$$

becomes

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P} dT + \left(\frac{\partial G}{\partial P}\right)_{T} dP$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \sum_{\substack{\text{all}\\ \text{components}}} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} dn_i$$

We can write

$$\left(\frac{\partial G}{\partial T}\right)_{P,n_i} = -S(T,\, P,\, n_i) \quad \text{and} \quad \left(\frac{\partial G}{\partial P}\right)_{T,n_i} = V(T,\, P,\, n_i)$$

Here we recognize explicitly that S and V also are functions of the mole numbers as well as functions of T and P. The partial derivative of G with respect to the mole number n_i at constant T and P and mole numbers $n_j \neq n_i$ is defined as

$$\boxed{\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \mu_i}$$

where μ_i is the chemical potential.

$$dG = -SdT + VdP + \sum_{\substack{\text{all}\\ \text{components}}} \mu_i dn_i$$

The Helmholtz free energy

$$A = G - PV$$

Therefore

$$dA = dG - PdV - VdP$$

$$dA = -PdV - SdT + \sum_{\substack{\text{all}\\ \text{components}}} \mu_i dn_i$$

Therefore, the chemical potential for the component i may also be defined as

$$\boxed{\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j}}$$

Similarly, we can show from other commonly used thermodynamic relationships that

$$\boxed{\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j}} \qquad \boxed{\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j}} \qquad \boxed{\mu_i = -\frac{1}{T}\left(\frac{\partial S}{\partial n_i}\right)_{U,V,n_j}}$$

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

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j} \qquad \mu_i = -\frac{1}{T}\left(\frac{\partial S}{\partial n_i}\right)_{U,V,n_j}$$

Because most chemical, biological, and geological processes occur at constant temperature and pressure, it is convenient to provide a special name for the partial derivatives of all thermodynamic properties with respect to mole number at constant pressure and temperature. They are called partial molar properties, and they are defined by the relationship

$$J_{\text{m}i} = \left(\frac{\partial J}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

where J is any thermodynamic property. The partial molar Gibbs function is the chemical potential. However, the following derivatives are partial molar properties, but they are not chemical potentials:

$$\left.\begin{aligned}
\left(\frac{\partial A}{\partial n_i}\right)_{T,P,n_j} &= A_{\text{m}i} \neq \mu_i \\
\left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_j} &= H_{\text{m}i} \neq \mu_i \\
\left(\frac{\partial U}{\partial n_i}\right)_{T,P,n_j} &= U_{\text{m}i} \neq \mu_i \\
\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_j} &= S_{\text{m}i} \neq -\frac{\mu_i}{T}
\end{aligned}\right\}$$

because chemical potentials are derivatives with respect to the mole numbers with the *natural independent variables* held constant.

CRITERIA OF EQUILIBRIUM AND SPONTANEITY IN SYSTEMS OF VARIABLE COMPOSITION

For systems having a fixed composition (closed systems) we already know that

$$dA \leq 0 \text{ (constant } T,\ V) \quad dG \leq 0 \text{ (constant } T,\ P)$$

These relations are valid for all closed systems in which only PdV work is performed. Similarly,

$dG \leq ðW_{\text{net}}$ (constant T, P)

is valid for all closed systems in which work other than pressure-volume work is performed. In this expression, the equality applies to a reversible process and the inequality applies to an irreversible process, whether the change of state is spontaneous or non-spontaneous.

If the change is spontaneous, $dG < 0$ (that is, dG is negative), and $ðW_{\text{net}} < 0$ (that is,$ðW_{\text{net}}$ is negative), so that in absolute magnitude, $|dG| \geq |ðW_{\text{net}}|$.

If the change of state is non-spontaneous, $dG > 0$ (that is, dG is positive), and $ðW_{\text{net}} > 0$ (that is,$ðW_{\text{net}}$ is positive), so that in absolute magnitude, $|dG| \leq |ðW_{\text{net}}|$.

Thus, for a spontaneous change of state, the magnitude of dG is equal to the maximum non-PV work that can be performed by the system, whereas, for a non-spontaneous change of state, the magnitude of dG is equal to the minimum non-PV work that must be performed on the system to bring about the change in state.

As G is a state function, the value of dG is the same for a given change of state, whether it is carried out reversibly or irreversibly; it is the value of dW that depends on reversibility.
If the T and P are constants, then from

$$dA = -PdV - SdT + \sum_{\substack{\text{all} \\ \text{components}}} \mu_i dn_i$$

we have

$$dG = \sum_i \mu_i dn_i$$

which means that the criteria for spontaneity and equilibrium become (when the only constraint on the system is the constant pressure of the atmosphere and only PdV work is performed)

$$\sum_i \mu_i dn_i \leq 0 \text{ (constant } T,\ P)$$

When the system is placed under additional constraints, the relationships for non-PdV work are

$$\sum_i \mu_i dn_i \leq ðW_{\text{net}} \text{ (constant } T,\ P)$$

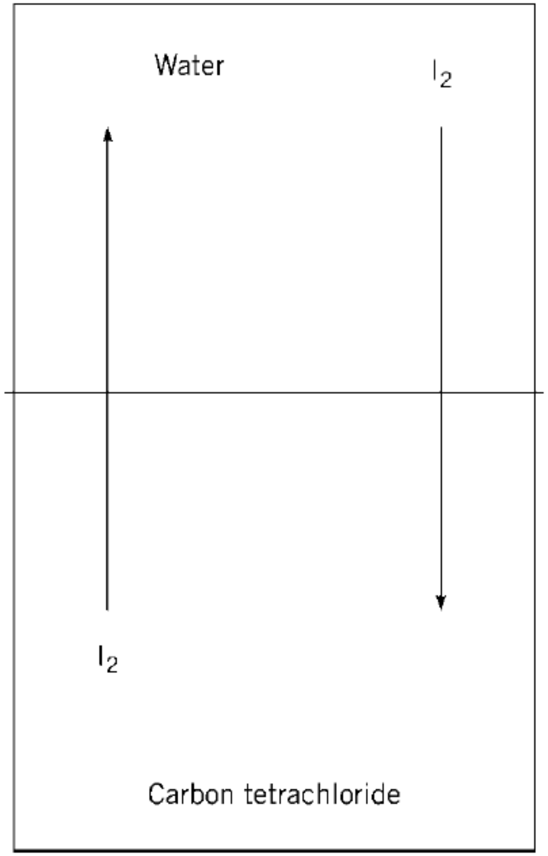
in which the equality applies to a reversible process and the inequality applies to an irreversible process.

The chemical potential for chemical, biological, or geological systems is analogous to the height, or gravitational potential, for a gravitational system; chemical, biological, or geological systems change spontaneously in the direction of decreasing chemical potential, just as an object in a gravitational field moves spontaneously in the direction of decreasing gravitational potential (downward).

ESCAPING TENDENCY

Chemical Potential and Escaping Tendency

G. N. Lewis proposed the term “escaping tendency” to give a strong kinetic-molecular flavor to the concept of the chemical potential. Let us consider two solutions of iodine, in water and carbon tetrachloride, which have reached equilibrium with each other at a fixed pressure and temperature .



In this system at equilibrium, let us carry out a transfer of an infinitesimal quantity of iodine from the water phase to the carbon tetrachloride phase. On the basis of

$$\sum_i \mu_i dn_i \leq 0 \text{ (constant } T,\ P)$$

we can say that

$$\mu_{I_2(H_2O)} dn_{I_2(H_2O)} + \mu_{I_2(CCl_4)} dn_{I_2(CCl_4)} = 0$$

In this closed system, any loss of iodine from the water phase is accompanied by an equivalent gain in the carbon tetrachloride thus,

$$-dn_{I_2(H_2O)} = dn_{I_2(CCl_4)}$$

Hence

$$\mu_{I_2(H_2O)}dn_{I_2(H_2O)} + \mu_{I_2(CCl_4)}[-dn_{I_2(H_2O)}] = 0$$

It follows that

$$\mu_{I_2(H_2O)} = \mu_{I_2(CCl_4)}$$

for this system in equilibrium at constant pressure and temperature. Thus, at equilibrium, the chemical potential of the iodine is the same in all phases in which it is present, or the escaping tendency of the iodine in the water is the same as that of the iodine in the carbon tetrachloride. We can return to the analogy with gravitational potential; stating that the iodine in the two phases have the same chemical potential is analogous to saying that two bodies at the same altitude have the same gravitational potential.

Homogeneous functions: Gibbs-Duhem relation

Say, $u(x,y) = ax^2 + bxy + cy^2$

$$\left.\begin{array}{l} x \to \lambda x \\ y \to \lambda y \end{array}\right\} \quad u^*(\lambda x, \lambda y) = a(\lambda x)^2 + b(\lambda x)(\lambda y) + c(\lambda y)^2 = \lambda^2(ax^2 + bxy + cy^2) = \lambda^2 u(x,y)$$

$\therefore$ $u(x,y)$ is a homogeneous function of degree 2.

Euler's theorem: If $f(x,y)$ is a homogeneous function of degree n, then

$$x\left(\frac{\partial f}{\partial x}\right)_y + y\left(\frac{\partial f}{\partial y}\right)_x = n f(x,y)$$

Homogeneous functions of degree 0 are called intensive properties.

" " " " 1 " " extensive " .

* a two-component system: n_1 and n_2 are the mole nos.

$$V = f(n_1, n_2)$$

applying Euler's theorem: $n_1\left(\frac{\partial V}{\partial n_1}\right)_{n_2} + n_2\left(\frac{\partial V}{\partial n_2}\right)_{n_1} = V$

$\therefore$ $V = n_1\bar{V}_1 + n_2\bar{V}_2$ $\quad \left.\begin{array}{l}\bar{V}_1\\ \bar{V}_2\end{array}\right\}$ partial molar vols. of components 1 and 2. $\quad V = \sum_{i=1}^{m} n_i \bar{V}_i$

* Gibbs free energy, $G = f(p, T, n_1, n_2)$ / $G = f(n_1, n_2)$ at const. p, T

applying Euler's theorem: $n_1\left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2} + n_2\left(\frac{\partial G}{\partial n_2}\right)_{p,T,n_1} = G$

$z = f(x,y)$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$\therefore$ $G_{p,T} = n_1\mu_1 + n_2\mu_2$

total differential of G at const. p, T

$$dG_{p,T} = n_1 d\mu_1 + \mu_1 dn_1 + n_2 d\mu_2 + \mu_2 dn_2 \quad \text{———} \ ①$$

alternatively, $G = f(n_1, n_2)$ at const. p, T

$$dG_{p,T} = \left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{p,T,n_1} dn_2 \quad \text{or,} \quad dG_{p,T} = \mu_1 dn_1 + \mu_2 dn_2 \quad \text{———} \ ②$$

Comparing ① and ②

$$n_1 d\mu_1 + n_2 d\mu_2 + \cancel{\mu_1 dn_1} + \cancel{\mu_2 dn_2} = \cancel{\mu_1 dn_1} + \cancel{\mu_2 dn_2}$$

$\boxed{n_1 d\mu_1 + n_2 d\mu_2 = 0}$ Gibbs-Duhem relation

* for any general multi-component system

$$\sum_{i=1}^{m} n_i d\mu_i = 0$$

Chemical equilibrium in a system of variable composition

Condition for eqm

$$\sum_i \mu_i dn_i \leq 0 \quad (\text{at const. } T, p)$$

is applied to a chemically reacting system.

$$aA + bB + \cdots \rightleftharpoons rR + sS + \cdots$$

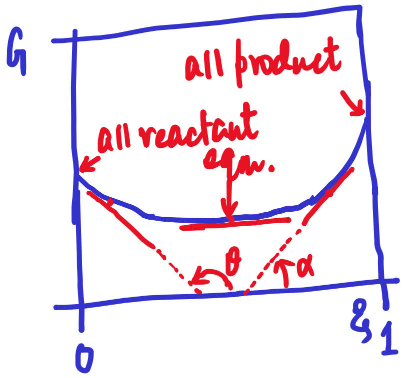
If this rxn. takes place at const. p, T

(a) $dG_{p,T} = \sum_i \mu_i dn_i$ and

(b) $\sum_i \mu_i dn_i \leq 0$

$\therefore$ At const. p, T

$$dG = \mu_A dn_A + \mu_B dn_B + \cdots + \mu_R dn_R + \mu_S dn_S + \cdots$$



dn's are not independent

$$-\frac{dn_A}{a} = -\frac{dn_B}{b} = \cdots = \frac{dn_R}{r} = \frac{dn_S}{s} = \cdots$$

ξ = extent of reaction

$$\therefore d\xi = -\frac{dn_A}{a} = -\frac{dn_B}{b} = \cdots = \frac{dn_R}{r} = \frac{dn_S}{s} = \cdots$$

$$\therefore dG = -a\mu_A d\xi - b\mu_B d\xi - \cdots + r\mu_R d\xi + s\mu_S d\xi + \cdots$$

$$= \left[(r\mu_R + s\mu_S + \cdots) - (a\mu_A + b\mu_B + \cdots)\right] d\xi$$

$$\therefore \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = (r\mu_R + s\mu_S + \cdots) - (a\mu_A + b\mu_B + \cdots)$$

HOMOGENEOUS FUNCTIONS AND THE GIBBS-DUHEM RELATION

In connection with the development of the thermodynamic concept of partial molar quantities, it is desirable to be familiar with a mathematical relationship known as Euler's theorem. As this theorem is stated with reference to "homogeneous" functions, we will consider briefly the nature of these functions.

Definition: As a simple example, let us consider the function

$$u(x,y) = ax^2 + bxy + cy^2$$

If we replace the variables x and y by λx and λy respectively, then we have the transformed function

$$u^*(\lambda x, \lambda y) = a(\lambda x)^2 + b(\lambda x)(\lambda y) + c(\lambda y)^2 = \lambda^2(ax^2 + bxy + cy^2) = \lambda^2 u(x,y)$$

We say that $u(x,y)$ is a homogeneous function of degree 2. Euler's theorem says that, for any homogeneous function, $f(x,y)$, of degree n,

$$x\left(\frac{\partial f}{\partial x}\right)_y + y\left(\frac{\partial f}{\partial y}\right)_x = nf(x,y)$$

Homogeneous functions of degree 0 and 1 are called intensive and extensive properties of a system. For example, the volume V, or the Gibbs free energy G of a system are extensive properties, while molar volume $\bar{V}$, or density ρ are intensive properties. Say, for a system having two components, with mole numbers n_1 and n_2, then, the volume of the system is

$$V = f(n_1, n_2)$$

Since volume is an extensive property, applying Euler's theorem, we have

$$n_1\left(\frac{\partial V}{\partial n_1}\right)_{n_2} + n_2\left(\frac{\partial V}{\partial n_2}\right)_{n_1} = V \Rightarrow n_1\bar{V}_1 + n_2\bar{V}_2 = V$$

where, $\bar{V}_1$ and $\bar{V}_2$ are the partial molar volumes of the two components. Similarly, the Gibbs free energy G is an extensive property. Thus, $G = f(p, T, n_1, n_2)$. Applying Euler's theorem at constant T and p, we have

$$n_1\left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2} + n_2\left(\frac{\partial G}{\partial n_2}\right)_{p,T,n_1} = G$$

$$\therefore G = n_1\mu_1 + n_2\mu_2$$

The total differential of G at constant T and p is

$$dG_{p,T} = n_1 d\mu_1 + n_2 d\mu_2 + \mu_1 dn_1 + \mu_2 dn_2 \qquad (1)$$

Also,

$$dG_{p,T} = \left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{p,T,n_1} dn_2$$

$$\text{or,} \quad dG_{p,T} = \mu_1 dn_1 + \mu_2 dn_2 \qquad (2)$$

Comparing Eqs. (1) and (2), we have

$$n_1 d\mu_1 + n_2 d\mu_2 + \mu_1 dn_1 + \mu_2 dn_2 = \mu_1 dn_1 + \mu_2 dn_2$$

$$\text{or,} \quad n_1 d\mu_1 + n_2 d\mu_2 \qquad (3)$$

Eq. (3) is called the Gibbs-Duhem equation. For a general multi-component system (say, having some n number of components), Gibbs-Duhem relation may be written as

$$\sum_{i=1}^{n} n_i d\mu_i = 0$$

CHEMICAL EQUILIBRIUM IN SYSTEMS OF VARIABLE COMPOSITION

We can apply the criterion of equilibrium expressed in

$$\sum_I \mu_i dn_i \leq 0 \text{ (constant } T, P)$$

to chemically reacting systems. Consider the reaction

$$aA + bB + \cdots = rR + sS + \cdots$$

in which all reactants and products are in the same phase. If this chemical reaction is at equilibrium at a fixed pressure and temperature, it follows from

$$dG = \sum_i \mu_i dn_i \text{ and } \sum_I \mu_i dn_i \leq 0 \text{ (constant } T, P)$$

that

$$dG = \mu_A dn_A + \mu_B dn_B + \cdots + \mu_R dn_R + \mu_S dn_S + \cdots = 0$$

However, the various dn's in the above equation are not independent, but, in view of the stoichiometry of the reaction, they must be related as follows:

$$-\frac{dn_A}{a} = -\frac{dn_B}{b} = \cdots = \frac{dn_R}{r} = \frac{dn_S}{s} = \cdots$$

As reactants disappear and products appear in the reaction, the corresponding dn's in the above equation have opposite signs. In view of the series of equalities in this equation, let us define a quantity $d\xi$ such that

$$d\xi = -\frac{dn_A}{a} = -\frac{dn_B}{b} = \cdots = \frac{dn_R}{r} = \frac{dn_S}{s} = \cdots = \frac{dn_i}{\nu_i}$$

in which ν_i is merely a generalized notation for the *dimensionless stoichiometric coefficients*, $-a$, $-b$, r, s, and so on. The quantity ξ is called the *extent of reaction* or the *progress variable*, and it has the dimensions of *amount of substance* and has the unit mol. Using the last equation,

$$dG = \mu_A dn_A + \mu_B dn_B + \cdots + \mu_R dn_R + \mu_S dn_S + \cdots = 0$$

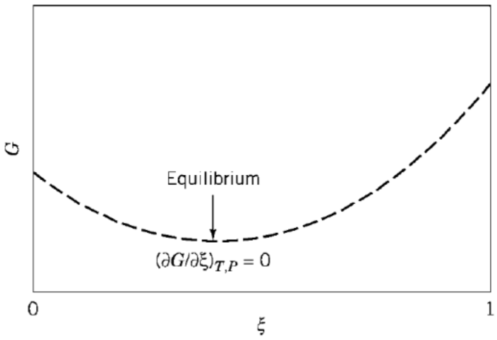
can be rewritten as

$$dG = -a\mu_A d\xi - b\mu_B d\xi - \cdots + r\mu_R d\xi + s\mu_S d\xi + \cdots = 0$$

Alternatively,

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = r\mu_R + s\mu_S - a\mu_A - b\mu_B = 0$$

is a criterion of equilibrium at constant temperature and pressure. The derivative $(\partial G/\partial \xi)_{T,P}$ is the slope of a plot of the Gibbs function of the system G against ξ, the progress variable. When $\xi = 0$, the system is all reactants, and when $\xi = 1$, the system is all products. At equilibrium, G is at a minimum, and the slope is equal to zero. If $(\partial G/\partial \xi)_{T,P} = r\mu_R + s\mu_S - a\mu_A - b\mu_B = 0$ is integrated with respect to ξ from $\xi = 0$ to $\xi = 1$ at constant values of the chemical potentials (fixed composition of the reacting mixture), then we obtain, at equilibrium,



$$\Delta G_m = G_{m2} - G_{m1} = \int_0^1 \left(\frac{\partial G}{\partial \xi}\right)_{T,P} d\xi = \sum_i \nu_i \mu_i = 0$$

in which it is understood that ν_i is a negative number for the stoichiometric coefficients of the reactants and a positive number for the products. The result is a molar quantity, because the integration leads to a mole of reaction in the sense given in the definition of mole. As the composition of the reacting mixture does not change when one mole of reaction occurs, we say that we are using an **"infinite copy model"**, which is a system so large that the conditions of constant composition are satisfied. Another way of writing the above equation is

$$\sum_i (|\nu_i|\mu_i)_{\text{reactants}} = \sum_i (|\nu_i|\mu_i)_{\text{products}}$$

The concept of escaping tendency also can be applied to the chemical reaction $aA + bB + \cdots = rR + sS + \cdots$. At equilibrium, from the above equation, we can say that the sum of the escaping tendencies of the reactants is equal to the sum of the escaping tendencies of the products. For a chemical transformation capable of undergoing a spontaneous change, it follows from

$$\sum_i \mu_i dn_i \leq 0 \text{ (constant } T, P) \text{ and } d\xi = -\frac{dn_A}{a} = -\frac{dn_B}{b} = \cdots = \frac{dn_R}{r} = \frac{dn_S}{s} = \frac{dn_i}{\nu_i} \text{ that } \sum_i \nu_i \mu_i < 0.$$

That is,

$$\sum_i (|\nu_i|\mu_i)_{\text{reactants}} > \sum_i (|\nu_i|\mu_i)_{\text{products}}$$

Thus, for a spontaneous reaction, we can say that the sum of the escaping tendencies for the reactants is greater than the sum of the escaping tendencies for the products.

THERMODYNAMICS OF OPEN SYSTEMS [SEMESTER-III (H); C5T]
Google Meet Link: https://meet.google.com/isc-odcs-gnw
Date: 05/01/2024

Mixtures of Ideal Gases

We define an ideal gas on the basis of two properties:

$$PV = nRT \text{ (equation of state) and } \left(\frac{\partial U}{\partial V}\right)_T = 0 \text{ (no interaction)}$$

We define an ideal gas mixture as one that follows Dalton's law:

$$P = n_1\frac{RT}{V} + n_2\frac{RT}{V} + \cdots = \frac{RT}{V}\sum_i n_i$$

$$\Delta S_{mixing} = \frac{Q_{rev}}{T} = -n_A R\ln X_A - n_B R\ln X_B = -\sum_i n_i R\ln X_i$$

As both X_A and X_B are less than 1, ΔS_{mixing} is a positive quantity. For the reversible mixing, the entropy change in the surroundings is equal, but opposite in sign, and the total entropy change is zero. If the mixing process were allowed to proceed irreversibly by puncturing the two pistons, ΔS for the system would be the same, but ΔS for the surroundings would be zero because no work would be performed and no heat would be exchanged. Thus, the total change in entropy for the irreversible process would be positive. Therefore,

$$\Delta G_{mixing} = n_A RT\ln X_A + n_B RT\ln X_B = \sum_i n_i RT\ln X_i$$

The Chemical Potential of a Component in an Ideal Gas Mixture

ΔG_{mixing} is also equal to the difference between the Gibbs free energies of the mixture and that of the pure gases (unmixed). Thus,

$$\Delta G_{mixing} = G_{mixture} - G_{pure\ gases} = [n_A\mu_A + n_B\mu_B]_{mixture} - [n_A\bar{G}_A^* + n_B\bar{G}_B^*]_{pure\ gases}$$

where any $\bar{G}_i^*$ is molar free energy of the pure gas i. From $(\partial G/\partial P)_T = V$ and $PV = nRT$ we can obtain for the change in Gibbs function in the isothermal expansion of an ideal gas:

$$\Delta G = nRT\ln\frac{P_2}{P_1}$$

If the change in state is the expansion of one mole of an ideal gas from a standard pressure $P^0 = 0.1$ MPa to a pressure P, then

$$\Delta G = \bar{G} - \bar{G}^0 = RT\ln(P/P^0) \Rightarrow \bar{G} = \bar{G}^0 + RT\ln(P/P^0)$$

Substituting for $\bar{G}$ from the above equation into the expression for ΔG_{mixing}:

$$\Delta G_{mixing} = n_A\mu_A + n_B\mu_B - n_A[\bar{G}_A^0 + RT\ln(P/P^0)] - n_B[\bar{G}_B^0 + RT\ln(P/P^0)]$$

From, $\Delta G_{mixing} = n_A RT\ln X_A + n_B RT\ln X_B$, and the last equation,

$$n_A RT\ln X_A + n_B RT\ln X_B = n_A\mu_A + n_B\mu_B - n_A[\bar{G}_A^0 + RT\ln(P/P^0)] - n_B[\bar{G}_B^0 + RT\ln(P/P^0)]$$

The coefficients of n_A and n_B on the two sides of the above equation must be equal. Hence,

$$RT\ln X_A = \mu_A - \bar{G}_A^0 - RT\ln(P/P^0)$$

$$\therefore \mu_A = \bar{G}_A^0 + RT\ln X_A + RT\ln(P/P^0) = \bar{G}_A^0 + RT\ln\left(\frac{PX_A}{P^0}\right)$$

and, similarly for μ_B. We shall define the partial pressure of an ideal gas as the product of the pressure of the gas and its mole fraction in the mixture. Thus, $p_A = PX_A$. Hence,

$$\mu_A = \bar{G}_A^0 + RT\ln\left(\frac{p_A}{P^0}\right)$$

We have seen that, $\Delta G = \bar{G} - \bar{G}^0 = RT\ln(P/P^0)$ which means that

$$\bar{G} = \bar{G}^0 + RT\ln(P/P^0)$$

This equation is of a form identical to the above expression for μ_A, which gives the chemical potential of a component of an ideal gas mixture, except that for the latter, partial pressure is substituted for total pressure. If the standard state of a component of the mixture is defined as one in which the partial pressure of that component is 0.1 MPa, then $\mu_A^0 = \bar{G}_A^0$ and we can write

$$\mu_A = \mu_A^0 + RT\ln\left(\frac{p_A}{P^0}\right)$$

Chemical Equilibrium in Ideal Gas Mixtures

Consider the reaction

$$aA(p_A) + bB(p_B) = rR(p_R) + sS(p_S)$$

in which all reactants and products are in the same phase.

We have already seen that at equilibrium,

$$\Delta\bar{G} = \bar{G}_2 - \bar{G}_1 = \int_0^1 \left(\frac{\partial G}{\partial \xi}\right)_{T,P} d\xi = \sum_i \nu_i \, \mu_i = 0$$

Therefore, for the above reaction,

$$\Delta\bar{G} = -a\mu_A - b\mu_B + r\mu_R + s\mu_S$$

Using $\mu_i = \mu_i^0 + RT\ln(p_i/P^0)$ in the above equation,

$$\Delta\bar{G} = -a[\mu_A^0 + RT\ln(p_A/P^0)] - b[\mu_B^0 + RT\ln(p_B/P^0)]$$
$$+r[\mu_R^0 + RT\ln(p_R/P^0)] + s[\mu_S^0 + RT\ln(p_S/P^0)] = 0$$
$$-a\mu_A^0 - b\mu_B^0 + r\mu_R^0 + s\mu_S^0 = aRT\ln(p_A/P^0) + bRT\ln(p_B/P^0) - rRT\ln(p_R/P^0) - sRT\ln(p_S/P^0)$$
$$-a\mu_A^0 - b\mu_B^0 + r\mu_R^0 + s\mu_S^0 = RT\ln(p_A/P^0)^a + RT\ln(p_B/P^0)^b - RT\ln(p_R/P^0)^r - RT\ln(p_S/P^0)^s$$

We define: $-a\mu_A^0 - b\mu_B^0 + r\mu_R^0 + s\mu_S^0 = \Delta\bar{G}^0$

$$\therefore \Delta\bar{G}^0 = -RT\ln\left[\frac{(p_R/P^0)^r (p_S/P^0)^s}{(p_A/P^0)^a (p_B/P^0)^b}\right]_{\mathrm{equilibrium}}$$

As $\Delta\bar{G}^0$ is a constant at constant T, the quantity in brackets is also a constant at constant T, and, in particular, independent of the total pressure and the initial composition of the system. We define the equilibrium constant in terms of partial pressures for a mixture of ideal gases, as

$$K_P = \left[\frac{(p_R/P^0)^r (p_S/P^0)^s}{(p_A/P^0)^a (p_B/P^0)^b}\right]_{\mathrm{equilibrium}}$$

The last two leads us to, $\Delta\bar{G}^0 = -RT\ln K_P$. The subscript P distinguishes the ideal gas equilibrium constant in terms of partial pressures from other forms for the constants that will be derived for real systems.

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Consider the reaction

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$$\Delta\bar{G} = -a[\mu_A^0 + RT\ln(p_A/P^0)] - b[\mu_B^0 + RT\ln(p_B/P^0)]$$
$$+r[\mu_R^0 + RT\ln(p_R/P^0)] + s[\mu_S^0 + RT\ln(p_S/P^0)] = 0$$

$$-a\mu_A^0 - b\mu_B^0 + r\mu_R^0 + s\mu_S^0 = aRT\ln(p_A/P^0) + bRT\ln(p_B/P^0) - rRT\ln(p_R/P^0) - sRT\ln(p_S/P^0)$$

$$-a\mu_A^0 - b\mu_B^0 + r\mu_R^0 + s\mu_S^0 = RT\ln(p_A/P^0)^a + RT\ln(p_B/P^0)^b - RT\ln(p_R/P^0)^r - RT\ln(p_S/P^0)^s$$

We define: $-a\mu_A^0 - b\mu_B^0 + r\mu_R^0 + s\mu_S^0 = \Delta\bar{G}^0$

$$\therefore \Delta\bar{G}^0 = -RT\ln\left[\frac{(p_R/P^0)^r(p_S/P^0)^s}{(p_A/P^0)^a(p_B/P^0)^b}\right]_{\text{equilibrium}}$$

As $\Delta\bar{G}^0$ is a constant at constant T, the quantity in brackets is also a constant at constant T, and, in particular, independent of the total pressure and the initial composition of the system. We define the equilibrium constant in terms of partial pressures for a mixture of ideal gases, as

$$K_P = \left[\frac{(p_R/P^0)^r(p_S/P^0)^s}{(p_A/P^0)^a(p_B/P^0)^b}\right]_{\text{equilibrium}}$$

The last two leads us to, $\Delta\bar{G}^0 = -RT\ln K_P$. The subscript P distinguishes the ideal gas equilibrium constant in terms of partial pressures from other forms for the constants that will be derived for real systems. Now, if we think of a situation that is not in equilibrium, then,

$$\Delta\bar{G} = -a[\mu_A^0 + RT\ln(p_A/P^0)] - b[\mu_B^0 + RT\ln(p_B/P^0)]$$
$$+r[\mu_R^0 + RT\ln(p_R/P^0)] + s[\mu_S^0 + RT\ln(p_S/P^0)]$$

and since the system is not at equilibrium, the RHS$\neq 0$.

$$\therefore \Delta\bar{G} = \left(r\mu_R^0 + s\mu_S^0 - a\mu_A^0 - b\mu_B^0\right) + RT\ln\left[\frac{(p_R/P^0)^r(p_S/P^0)^s}{(p_A/P^0)^a(p_B/P^0)^b}\right]_{\text{not at equilibrium}}$$

$$\text{or,}\ \ \Delta\bar{G} = \Delta\bar{G}^0 + RT\ln\left[\frac{(p_R/P^0)^r(p_S/P^0)^s}{(p_A/P^0)^a(p_B/P^0)^b}\right]_{\text{not at equilibrium}} = \Delta\bar{G}^0 + RT\ln Q^*$$

where, Q^* for the quotient of pressures not at equilibrium, that is,

$$Q^* = \left[\frac{(p_R/P^0)^r(p_S/P^0)^s}{(p_A/P^0)^a(p_B/P^0)^b}\right]_{\text{not at equilibrium}}$$

$$\therefore \Delta\bar{G} = \Delta\bar{G}^0 + RT\ln Q^* = -RT\ln K_P + RT\ln Q^* = RT\ln(Q^*/K_P)$$

Thus, if the initial quotient of pressures is greater than K_P, ΔG_{m} is positive and the reaction will be spontaneous to the left. Whereas if the initial quotient of pressures is less than K_P, ΔG_{m} is negative and the reaction will be spontaneous to the right. Now, from

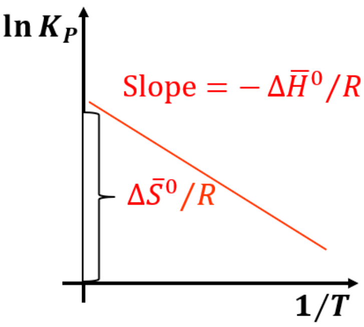
$$K_P = \left[\frac{(p_R/P^0)^r(p_S/P^0)^s}{(p_A/P^0)^a(p_B/P^0)^b}\right]_{\text{equilibrium}}$$

we conclude that:

1. The equilibrium constant, K_P is a dimensionless quantity, and
2. Also, that K_P depends on the choice of standard state, but not on the units used to describe the standard state pressure.

The equilibrium constant has the same value whether P° is expressed as 750.062 Torr, 0.98692 atm, 0.1 MPa, or 1 bar.

How does the equilibrium constant K_P depend on T?



We have seen that

$$\Delta\bar{G}^0 = -RT\ln K_P$$

and, also

$$\Delta\bar{G}^0 = \Delta\bar{H}^0 - T\Delta\bar{S}^0$$

Therefore,

$$-RT\ln K_P = \Delta\bar{H}^0 - T\Delta\bar{S}^0$$

so that,

$$\ln K_P = \left(-\frac{\Delta\bar{H}^0}{R}\right)\frac{1}{T} + \frac{\Delta\bar{S}^0}{R}$$

A plot of $\ln K_P$ (along Y axis) against $1/T$ (along X axis) will give a straight line with a slope of $(-\Delta\bar{H}^0/R)$ and a Y intercept of $\Delta\bar{S}^0/R$. From the Gibbs-Helmholtz relation,

$$\left[\frac{\partial(\Delta\bar{G}^0/T)}{\partial T}\right]_P = -\frac{\Delta\bar{H}^0}{T^2}$$

so that,

$$\frac{d}{dT}\left[\frac{\Delta\bar{G}^0}{T}\right]_P = -\frac{\Delta\bar{H}^0}{T^2}$$

since both K_P and $\Delta\bar{G}^0$ are independent of P. Therefore, from

$$\Delta\bar{G}^0 = -RT\ln K_P$$

we can write,

$$\frac{d}{dT}\left[-\frac{RT\ln K_P}{T}\right]_P = -\frac{\Delta\bar{H}^0}{T^2}$$

$$\therefore \frac{d\ln K_P}{dT} = \frac{\Delta\bar{H}^0}{RT^2} \Rightarrow \left\{\frac{d\ln K_P}{d(1/T)}\right\} = -\frac{\Delta\bar{H}^0}{R}$$

This equation is known as van't Hoff equation. For an endothermic reaction, $\Delta\bar{H}^0 > 0$, and the RHS is positive, so that $\ln K_P$ (and also K_P) increases with increase in temperature. For an exothermic reaction, $\Delta\bar{H}^0 < 0$, and the RHS is negative, so that $\ln K_P$ (and also K_P) decreases with increase in temperature.

THE FUGACITY FUNCTION OF A PURE REAL GAS

We have expressed the molar free energy of an idea gas as

$$\bar{G} = \bar{G}^0 + RT\ln P/P^0$$

using the ideal gas equation of state $V = nRT/P$ and the standard relation $(\partial G/\partial P)_T = V$ by solving the integral

$$\Delta G = \int_{P^\circ}^{P} V dP = \int_{P^\circ}^{P} \frac{nRT}{P} dP$$

Similarly, we obtained the chemical potential of a component of an ideal gas mixture as

$$\mu_A = \mu_A^0 + RT\ln p_A/P^0$$

from an analysis of the van't Hoff mixing experiment, using the same integral. Is it possible to obtain similar expressions for systems of real gases? G. N. Lewis: Defined a new function, the fugacity f, with a universal relationship to the chemical potential, and let the dependence of f on P vary for different gases. The fugacity is defined to have the dimensions of pressure. An advantage of the f over μ as a measure of escaping tendency is that an absolute value of the fugacity can be calculated, whereas an absolute value of the chemical potential cannot be calculated. One part of the definition of fugacity can be stated as

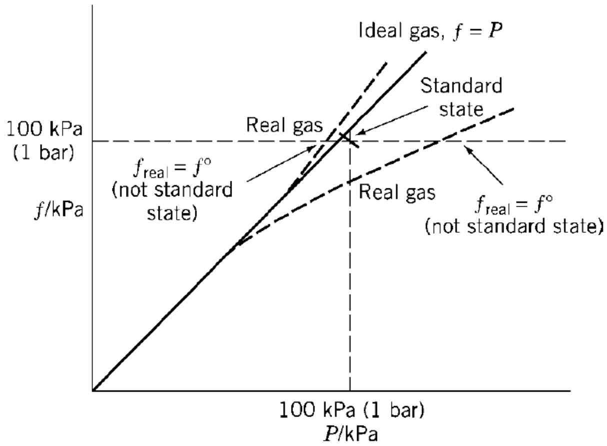
$$\mu = \mu^0 + RT\ln(f/f^0)$$

in which μ^0 is a function of T only, that is, $\mu^0 = \mu^0(T)$. The standard chemical potential is characteristic of each gas and the standard state chosen. For a pure gas, the value of f^0 is chosen equal to P^0, 0.1

MPa. As all gases approach ideality as their pressure is decreased, and as the above equation is of the same form as the one for an ideal gas, it is convenient to complete the definition of f by stating that,

$$\lim_{P\to 0} f/P = 1$$

That is, as the pressure approaches zero, the fugacity approaches the pressure.



The standard state for a real gas is chosen as the state at which the f is equal to 0.1 MPa, 1 bar, along a line extrapolated from values of f at low pressure. The standard state for a real gas is then a hypothetical 0.1 MPa standard state. Therefore, from $\mu = \mu^0 + RT\ln(f/f^0)$, we can see that the change in the Gibbs function for the isothermal expansion of a real gas is,

$$\Delta G = nRT\ln(f_2/f_1).$$

As the pressure approaches zero, $\lim_{P\to 0} f/P = 1$ applies, and ΔG approaches the value calculated from $\Delta G = nRT\ln(P_2/P_1)$. Therefore, from $\Delta G = nRT\ln(f_2/f_1)$, which for one mole may be expressed as $d\bar{G} = RTd\ln f$, and

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = \left(\frac{\partial \bar{G}_i}{\partial P}\right)_T = \bar{V}_i,$$

we can write,

$$\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{\bar{V}}{RT}$$

since f^0 is independent of P.

Change of Fugacity with Temperature

Let us consider an isothermal process in which a gas is transformed form one state A at a pressure P to another A^* at a different pressure P^*. Such a transformation can be represented as follows:

$$A(P) = A^*(P^*)$$

The change in the Gibbs function for such a transformation is given by the expression

$$\Delta G_m = \mu^* - \mu = RT\ln\left(f^*/f^{\circ}\right) - RT\ln\left(f/f^{\circ}\right) = RT\ln(f^*/f)$$

so that

$$\frac{\mu^*}{T} - \frac{\mu}{T} = R\ln(f^*/f)$$

Change of fugacity with temperature

a system of gas; isothermal transformation from

$$A(p) \rightarrow A^*(p^*)$$

$\Delta G_m = \mu^* - \mu = RT\ln(f^*/f^0) - RT\ln(f/f^0)$

f^0 = standard fugacity of the system

μ^0's are functions of T only; same for both the states; cancel eachother out

$$\therefore \mu^* - \mu = RT\ln(f^*/f) \quad \text{or,} \quad \frac{\mu^*}{T} - \frac{\mu}{T} = R\ln(f^*/f) \text{ — ①}$$

Now, $dG = Vdp - SdT$ or, $(\partial G/\partial T)_p = -S$

for a mole of substance, $(\partial G_m/\partial T)_p = -S_m$ or, $\boxed{(\partial\mu/\partial T)_p = -S_m}$

Also, $G_m = H_m - TS_m$ or, $\mu = H_m - TS_m$ or, $\frac{\mu}{T} = \frac{H_m}{T} - S_m$

$$\frac{\mu}{T} = \frac{H_m}{T} + \left(\frac{\partial\mu}{\partial T}\right)_p$$

$$\text{or,} \left(\frac{\partial\mu}{\partial T}\right)_p - \frac{\mu}{T} = -\frac{H_m}{T} \quad \text{or,} \quad \frac{1}{T}\left(\frac{\partial\mu}{\partial T}\right)_p - \frac{\mu}{T^2} = -\frac{H_m}{T^2}$$

$$\text{or,} \left[\frac{\partial(\mu/T)}{\partial T}\right]_p = -\frac{H_m}{T^2}$$

$$\therefore \text{from ①} \quad \left[\frac{\partial(\mu^*/T)}{\partial T}\right]_{p^*} - \left[\frac{\partial(\mu/T)}{\partial T}\right]_p = R\left(\frac{\partial\ln f^*}{\partial T}\right)_{p^*} - R\left(\frac{\partial\ln f}{\partial T}\right)_p$$

$$R\left(\frac{\partial\ln f^*}{\partial T}\right)_{p^*} - R\left(\frac{\partial\ln f}{\partial T}\right)_p = -\frac{H_m^*}{T^2} + \frac{H_m}{T^2}$$

$$\left(\frac{\partial\ln f^*}{\partial T}\right)_{p^*} - \left(\frac{\partial\ln f}{\partial T}\right)_p = -\frac{H_m^*}{RT^2} + \frac{H_m}{RT^2}$$

If $p^* \to 0$, $f^* \to p^*$, $f^*/p^* \to 1$

$$\left.\left(\frac{\partial\ln f^*}{\partial T}\right)_{p^*} = \left(\frac{\partial\ln p^*}{\partial T}\right)_{p^*} = 0 \right\} \quad -\left(\frac{\partial\ln f}{\partial T}\right)_p = -\frac{H_m^*}{RT^2} + \frac{H_m}{RT^2}$$

$$\boxed{\left(\frac{\partial\ln f}{\partial T}\right)_p = \frac{H_m^* - H_m}{RT^2}}$$

$$\left[\frac{\partial(H_m^* - H_m)}{\partial p}\right]_T = \left(\frac{\partial H_m^*}{\partial p}\right)_T - \left(\frac{\partial H_m}{\partial p}\right)_T = -\left(\frac{\partial H_m}{\partial p}\right)_T$$

$$\left(\frac{\partial H_m}{\partial p}\right)_T = -C_{p_m}\mu_{JT}$$

$$\left[\frac{\partial(H_m^* - H_m)}{\partial p}\right]_T = C_{p_m}\mu_{JT} \rightarrow$$

pressure dependence of the change in the molar enthalpy of the system.

Helmholtz free energy change, ΔA, for n moles of a van der Waals gas

$$dA = -p\,dV - S\,dT \Rightarrow (\partial A/\partial V)_T = -p \quad \text{or, } dA = -p\,dV \; (T \text{ constant})$$

$$\left(p + \frac{n^2a}{V^2}\right)(V-nb) = nRT \quad \text{or, } p = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$$

$$dA = -\left(\frac{nRT}{V-nb} - \frac{n^2a}{V^2}\right)dV \quad \therefore \Delta A = -\int_{V_1}^{V_2}\left(\frac{nRT}{V-nb} - \frac{n^2a}{V^2}\right)dV$$

$$\text{or, } \Delta A = -\int_{V_1}^{V_2}\frac{nRT}{V-nb}\,dV + \int_{V_1}^{V_2}\frac{n^2a}{V^2}\,dV = -nRT\ln\frac{V_2-nb}{V_1-nb} - n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

Gibbs free energy change, ΔG for n moles of a van der Waals gas

$$dG = V\,dp - S\,dT \Rightarrow (\partial G/\partial p)_T = V \quad \text{or, } dG = V\,dp \; (T \text{ constant})$$

$$p = \frac{nRT}{V-nb} - \frac{n^2a}{V^2} \Rightarrow dp = -\frac{nRT}{(V-nb)^2}\,dV + \frac{2n^2a}{V^3}\,dV$$

$$\therefore V\,dp = -\frac{nRTV}{(V-nb)^2}\,dV + \frac{2n^2a}{V^2}\,dV$$

$$\Delta G = \int dG = \int_{V_1}^{V_2} V\,dp = -nRT\int_{V_1}^{V_2}\frac{V}{(V-nb)^2}\,dV + 2n^2a\int_{V_1}^{V_2}\frac{1}{V^2}\,dV$$

$$\Delta G = -nRT\ln\frac{V_2-nb}{V_1-nb} + n^2bRT\left(\frac{1}{V_2-nb} - \frac{1}{V_1-nb}\right) - 2n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

Compressibility factor, $Z = \frac{V_{m,r}}{V_{m,i}}$

$\Delta G = nRT\ln(p_2/p_1) \longrightarrow \Delta G = nRT\ln(f_2/f_1)$

$$\Delta G_m = \int_{p_1}^{p_2} V_m dp = \Delta\mu$$

$$\int_{p_1}^{p_2} V_{m,i}\, dp = \mu_{p_2,i} - \mu_{p_1,i} = RT\ln(p_2/p_1) \text{ —— } ①$$

$$\int_{p_1}^{p_2} V_{m,r}\, dp = \mu_{p_2,r} - \mu_{p_1,r} = RT\ln(f_2/f_1) \text{ —— } ②$$

② − ①
$$\int_{p_1}^{p_2} (V_{m,r} - V_{m,i})\, dp = RT\ln \frac{f_2}{f_1}\cdot\frac{p_1}{p_2}$$

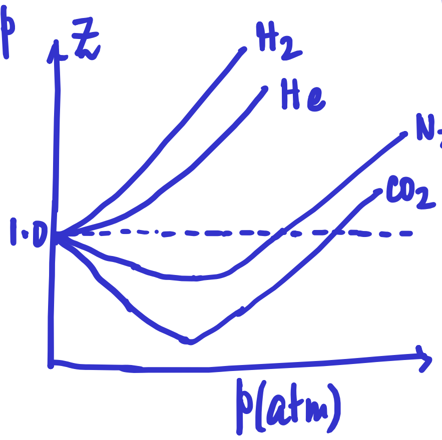
If $p_1 \to 0$, $\lim_{p_1\to 0} (f_1/p_1) = 1$

$$Z = \frac{V_{m,r}}{V_{m,i}}$$

$$V_{m,r} = Z V_{m,i} = Z\frac{RT}{p}$$

$$RT\ln(f_2/p_2) = \int_0^{p_2} (V_{m,r} - V_{m,i})\, dp$$

$$\boxed{\ln(f_2/p_2) = \int_0^{p_2} \frac{Z-1}{p}\, dp}$$



Change of Fugacity with Temperature

Let us consider an isothermal process in which a gas is transformed form one state A at a pressure P to another A^* at a different pressure P^*. Such a transformation can be represented as follows:

$$A(P) = A^*(P^*)$$

The change in the Gibbs function for such a transformation is given by the expression

$$\Delta G_m = \mu^* - \mu = RT\ln\left(f^*/f^\circ\right) - RT\ln\left(f/f^\circ\right) = RT\ln(f^*/f)$$

so that

$$\frac{\mu^*}{T} - \frac{\mu}{T} = R\ln(f^*/f)$$

The partial derivative of the fugacity with respect to temperature is given by

$$\left[\frac{\partial(\mu^*/T)}{\partial T}\right]_{P^*} - \left[\frac{\partial(\mu/T)}{\partial T}\right]_P = R\left(\frac{\partial\ln f^*}{\partial T}\right)_{P^*} - R\left(\frac{\partial\ln f}{\partial T}\right)_P$$

Now, we know that

$$G_\mathrm{m} = H_\mathrm{m} - TS_\mathrm{m} \Rightarrow \mu = H_\mathrm{m} - TS_\mathrm{m} \Rightarrow \frac{\mu}{T} = \frac{H_\mathrm{m}}{T} - S_\mathrm{m}$$

Now, since, $(\partial G/\partial T)_P = -S \Rightarrow (\partial\mu/\partial T)_P = -S_\mathrm{m}$

$$\therefore \frac{\mu}{T} = \frac{H_\mathrm{m}}{T} + \left(\frac{\partial\mu}{\partial T}\right)_P \Rightarrow \left(\frac{\partial\mu}{\partial T}\right)_P - \frac{\mu}{T} = -\frac{H_\mathrm{m}}{T}$$

$$\frac{1}{T}\left(\frac{\partial\mu}{\partial T}\right)_P - \frac{\mu}{T^2} = -\frac{H_\mathrm{m}}{T^2} \Rightarrow \left[\frac{\partial(\mu/T)}{\partial T}\right]_P = -\frac{H_\mathrm{m}}{T^2}$$

Therefore, from

$$\left[\frac{\partial(\mu^*/T)}{\partial T}\right]_{P^*} - \left[\frac{\partial(\mu/T)}{\partial T}\right]_P = R\left(\frac{\partial\ln f^*}{\partial T}\right)_{P^*} - R\left(\frac{\partial\ln f}{\partial T}\right)_P$$

and

$$\left[\frac{\partial(\mu/T)}{\partial T}\right]_P = -\frac{H_\mathrm{m}}{T^2}$$

we have,

$$\left[\frac{\partial(\mu^*/T)}{\partial T}\right]_{P^*} - \left[\frac{\partial(\mu/T)}{\partial T}\right]_P = -\frac{H^*_\mathrm{m}}{T^2} + \frac{H_\mathrm{m}}{T^2}$$

$$\therefore \left(\frac{\partial\ln f^*}{\partial T}\right)_{P^*} - \left(\frac{\partial\ln f}{\partial T}\right)_P = -\frac{H^*_\mathrm{m}}{RT^2} + \frac{H_\mathrm{m}}{RT^2}$$

If the pressure P^* approaches zero, the ratio of the fugacity to the pressure approaches one, and we can write

$$\left(\frac{\partial\ln f^*}{\partial T}\right)_{P^*} = \left(\frac{\partial\ln P^*}{\partial T}\right)_{P^*} = 0$$

Therefore, from

$$\therefore \left(\frac{\partial\ln f^*}{\partial T}\right)_{P^*} - \left(\frac{\partial\ln f}{\partial T}\right)_P = -\frac{H^*_\mathrm{m}}{RT^2} + \frac{H_\mathrm{m}}{RT^2}$$

and

$$\left(\frac{\partial\ln f^*}{\partial T}\right)_{P^*} = \left(\frac{\partial\ln P^*}{\partial T}\right)_{P^*} = 0$$

we can write,

$$\left(\frac{\partial\ln f}{\partial T}\right)_P = \frac{H^*_\mathrm{m} - H_\mathrm{m}}{RT^2}$$

in which H^*_m is the partial molar enthalpy of the substance in State A^*, that is, the state of zero pressure. Therefore, the difference $(H^*_\mathrm{m} - H_\mathrm{m})$ is the change in molar enthalpy when the gas goes from State A to its state of zero pressure, that is, at infinite volume. The pressure dependence of this enthalpy change is given by the expression

$$\left[\frac{\partial(H_{\mathrm{m}}^{*}-H_{\mathrm{m}})}{\partial P}\right]_T=-\left(\frac{\partial H_{\mathrm{m}}}{\partial P}\right)_T$$

because, $(\partial H_{\mathrm{m}}^{*}/\partial P)_T=0$, as H_{m}^{*} is the partial molar enthalpy at a fixed (zero) pressure. $(\partial H_{\mathrm{m}}/\partial P)_T$ is called the pressure coefficient of molar enthalpy. We know, from the Joule-Thomson (JT) effect, that the pressure coefficient of molar enthalpy, $(\partial H_{\mathrm{m}}/\partial P)_T$, is related to the JT coefficient, μ_{JT} by the relation

$$\left(\frac{\partial H_{\mathrm{m}}}{\partial P}\right)_T=-C_{P\mathrm{m}}\mu_{JT}$$

Therefore, combining

$$\left[\frac{\partial(H_{\mathrm{m}}^{*}-H_{\mathrm{m}})}{\partial P}\right]_T=-\left(\frac{\partial H_{\mathrm{m}}}{\partial P}\right)_T \text{ and} \left(\frac{\partial H_{\mathrm{m}}}{\partial P}\right)_T=-C_{P\mathrm{m}}\mu_{JT}$$

we get,

$$\left[\frac{\partial(H_{\mathrm{m}}^{*}-H_{\mathrm{m}})}{\partial P}\right]_T=C_{P\mathrm{m}}\mu_{JT}.$$

Because of this relationship between $(H_{\mathrm{m}}^{*}-H_{\mathrm{m}})$ and μ_{JT}, the former quantity frequently is referred to as the Joule-Thomson enthalpy. The pressure coefficient of this JT enthalpy change can be calculated from the known values of the JT coefficient and the heat capacity of the gas. Similarly, as $(H_{\mathrm{m}}^{*}-H_{\mathrm{m}})$ is a derived function of the fugacity, knowledge of the temperature dependence of the latter can be used to calculate the JT coefficient. As the fugacity and the JT coefficient are both measures of the deviation of a gas from ideality, it is not surprising that they are related.

A quick recap of some results for a system of van der Waals gas:

From the definition of Helmholtz free energy, the total infinitesimal change in it is $dA=-PdV-SdT$, so that $(\partial A/\partial V)_T=-P\Rightarrow dA=-PdV$ (T constant). For a system of n moles of a van der Waals gas, we have

$$dA=-\left(\frac{nRT}{V-nb}-\frac{n^2a}{V^2}\right)dV$$

$$\therefore \Delta A=-\int_{V_1}^{V_2}\frac{nRT}{V-nb}dV+\int_{V_1}^{V_2}\frac{n^2a}{V^2}dV=-nRT\ln\frac{V_2-nb}{V_1-nb}-n^2a\left(\frac{1}{V_2}-\frac{1}{V_1}\right)$$

From the definition of Gibbs free energy, the total infinitesimal change in it is $dG=VdP-SdT$, so that $(\partial G/\partial P)_T=V\Rightarrow dG=VdP$ (T constant). While evaluating the integral, it is convenient to replace dP in terms of dV. The van der Waals equation of state is

$$P=\frac{nRT}{V-nb}-\frac{n^2a}{V^2}\Rightarrow dP=-\frac{nRT}{(V-nb)^2}dV+\frac{2n^2a}{V^3}dV$$

$$\therefore VdP=-\frac{nRTV}{(V-nb)^2}dV+\frac{2n^2a}{V^2}dV$$

Therefore,

$$\Delta G=\int_{V_1}^{V_2}VdP=-nRT\int_{V_1}^{V_2}\frac{V}{(V-nb)^2}dV+2n^2a\int_{V_1}^{V_2}\frac{1}{V^2}dV$$

$$\text{or, }\Delta G=-nRT\int_{V_1}^{V_2}\frac{V-nb+nb}{(V-nb)^2}dV+2n^2a\int_{V_1}^{V_2}\frac{1}{V^2}dV$$

$$\text{or, }\Delta G=-nRT\int_{V_1}^{V_2}\frac{1}{V-nb}dV-nRT\int_{V_1}^{V_2}\frac{nb}{(V-nb)^2}dV+2n^2a\int_{V_1}^{V_2}\frac{1}{V^2}dV$$

$$\therefore \Delta G=-nRT\ln\frac{V_2-nb}{V_1-nb}+n^2bRT\left(\frac{1}{V_2-nb}-\frac{1}{V_1-nb}\right)-2n^2a\left(\frac{1}{V_2}-\frac{1}{V_1}\right)$$

Therefore, we have determined the total changes in A and G for a system composed of n moles of a van der Waals gas under an isothermal reversible expansion of the gas from V_1 to V_2.

We have seen from the definition of Gibbs free energy, the total infinitesimal change in it is $dG = VdP - SdT$, so that $(\partial G/\partial P)_T = V \Rightarrow dG = VdP$ (T constant). Note that, the above form of dG is absolutely general and is applicable for all substances. Also, from $\mu = \mu^\circ + RT\ln(f/f^\circ)$, we can see that the change in the Gibbs function for the isothermal expansion of a real gas is,

$$\Delta G = nRT\ln(f_2/f_1),$$

which for a mole becomes, $\Delta\mu = \mu_2 - \mu_1 = nRT\ln(f_2/f_1)$. Therefore, let us separately calculate ΔG for a mole of an ideal and a real gas, by noting that in general

$$\Delta G_\mathrm{m} = \int_{P_1}^{P_2} V_\mathrm{m} dP = \Delta\mu$$

Thus, we have

$$\int_{P_1}^{P_2} V_{\mathrm{m,\ ideal}} dP = \mu_{P_2,\ \mathrm{ideal}} - \mu_{P_1,\ \mathrm{ideal}} = RT\ln\frac{P_2}{P_1}$$

and

$$\int_{P_1}^{P_2} V_{\mathrm{m,\ real}} dP = \mu_{P_2,\ \mathrm{real}} - \mu_{P_1,\ \mathrm{real}} = RT\ln\frac{f_2}{f_1}$$

Taking the difference, we have

$$\int_{P_1}^{P_2} \left(V_{\mathrm{m,\ real}} - V_{\mathrm{m,\ ideal}}\right) dP = RT\ln\frac{f_2}{f_1} - RT\ln\frac{P_2}{P_1}$$

so that,

$$RT\ln\left(\frac{f_2}{f_1}\right)\left(\frac{P_1}{P_2}\right) = \int_{P_1}^{P_2} \left(V_{\mathrm{m,\ real}} - V_{\mathrm{m,\ ideal}}\right) dP$$

Let P_1 be allowed to approach zero, so that, $\lim\limits_{P_1\to 0} f_1/P_1 = 1$, hence

$$RT\ln\left(\frac{f_2}{P_2}\right) = \int_{0}^{P_2} \left(V_{\mathrm{m,\ real}} - V_{\mathrm{m,\ ideal}}\right) dP$$

Now, for a real gas,

$$V_{\mathrm{m,\ real}} = Z\frac{RT}{P} = ZV_{\mathrm{m,\ ideal}}$$

where Z is the compressibility factor of the gas. Therefore, from

$$RT\ln\left(\frac{f_2}{P_2}\right) = \int_{0}^{P_2} \left(V_{\mathrm{m,\ real}} - V_{\mathrm{m,\ ideal}}\right) dP$$

and,

$$V_{\mathrm{m,\ real}} = Z\frac{RT}{P} = ZV_{\mathrm{m,\ ideal}}$$

we have,

$$\ln\left(\frac{f_2}{P_2}\right) = \int_{0}^{P_2} \frac{Z-1}{P} dP$$

The integral over P in the above expression may be performed

(a) if the data for Z (or V_m) are available, or
(b) if the analytical expression for $Z(T,P)$ (or V_m in terms of P) is available.

In general, the value of f depends upon the value of Z. If Z is less than one, the RHS of the above equation will be negative and hence f_2 will be smaller than P_2. If Z is greater than one, the RHS of the above equation will be positive and hence f_2 will be greater than P_2.

Some examples of variation of fugacity with T

① Equation of state: $p(v_m - b) = RT$

$$\ln\left(\frac{f}{p}\right) = \int_0^p \frac{z-1}{p}\,dp$$

or, $V_m = b + \frac{RT}{p}$

Compressibility factor, $z = \frac{V_m}{V_{m,i}} = \frac{V_m}{RT/p} = \frac{pV_m}{RT}$

$\therefore z = \frac{p}{RT}\left(b + \frac{RT}{p}\right) = 1 + b\frac{p}{RT} \Rightarrow z - 1 = b\frac{p}{RT}$

$\therefore \ln\left(\frac{f}{p}\right) = \int_0^p \frac{z-1}{p}\,dp = \int_0^p \frac{1}{p}\,b\,\frac{p}{RT}\,dp = \frac{bp}{RT}$

$\therefore f/p = \exp\left(\frac{bp}{RT}\right)$

If bp/RT is small (when T is large; when p is small; or both)

$$\frac{f}{p} = \exp\left(\frac{bp}{RT}\right) = 1 + \frac{bp}{RT} + \frac{1}{2!}\left(\frac{bp}{RT}\right)^2 + \frac{1}{3!}\left(\frac{bp}{RT}\right)^3 + \cdots \simeq 1 + \frac{bp}{RT} = \frac{RT + bp}{RT}$$

$\therefore$ Eqn. of state: $pV_m = RT + bp$

$\therefore \frac{f}{p} = \frac{pV_m}{RT} = \frac{p}{p_i}$ or, $p^2 = fp_i$ $\therefore p = \sqrt{fp_i}$

$\Rightarrow$ the pressure of the gas is the geometric mean of the ideal pressure and the fugacity.

② fugacity, $f = p + \alpha p^2$, $\alpha = f(T)$ α is a function of T only.

$f = p + \alpha p^2$ or, $\frac{f}{p} = 1 + \alpha p$ or, $\ln\left(\frac{f}{p}\right) = \ln(1 + \alpha p)$

$\because \ln\left(\frac{f}{p}\right) = \int_0^p \frac{z-1}{p}\,dp$ $\therefore \ln(1+\alpha p) = \int_0^p \frac{z-1}{p}\,dp$

$\ln(1+\alpha p) = \int_0^p \frac{\alpha}{1+\alpha p}\,dp$ so that, $\int_0^p \frac{\alpha}{1+\alpha p}\,dp = \int_0^p \frac{z-1}{p}\,dp$

$\therefore \frac{\alpha}{1+\alpha p} = \frac{z-1}{p}$ or, $\frac{\alpha}{1+\alpha p} = \frac{(V_m/V_{m,i}) - 1}{p} = \frac{(pV_m/RT) - 1}{p}$

$$\frac{pV_m}{RT} = 1 + \frac{\alpha p}{1+\alpha p}$$

Thermodynamics of solutions

Solution: homogeneous mixture of more than one components

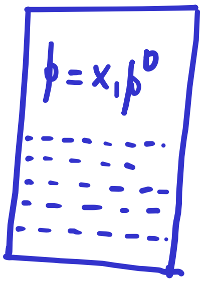
two components : binary → solvent(1) (component present in larger proportion)
→ solute(2) (component present in smaller amount)

three " : ternary

four " : quaternary

....

Solution: volatile solvent + non-volatile solute
(appreciable vap. press. at ordinary T)



T constant

vap. press. of the pure solvent $= p^0$ at T

vap. " " " solvent in soln. $= p$ at T

$p^0 > p$; lowering of vap. press., $p^0 - p$

relative lowering of vap. press. $\boxed{\frac{p^0 - p}{p^0} = x_2}$ = mol fraction of the solute

provided the solution is extremely dilute.

$$x_2 = \frac{n_2}{n_1+n_2} \; ; \; x_1 = \frac{n_1}{n_1+n_2} \Rightarrow x_1 + x_2 = 1$$

$\boxed{p = x_1 p^0}$ Raoult's law.

If the soln is in equm. with its vapour

$$\mu_{liq} = \mu_{vap}$$

μ_{liq} = chem. pot. of the solvent in the liq. phase

μ_{vap} = " " " " " " " vap. "

Now, $\mu_{vap} = \mu^0_{vap} + RT \ln p$ (assuming that the vap. phase behaves ideally)

$p = x_1 p^0$

$$\therefore \mu_{liq} = \mu^0_{vap} + RT\ln p$$
$$= \left(\mu^0_{vap} + RT\ln p^0\right) + RT\ln x_1$$
$$= \mu^0_{liq} + RT\ln x_1$$

$$\boxed{\mu = \mu^0 + RT\ln x}$$

Chem. pot. of the pure solvent.

Example 1

Say we have an equation of state for a gas which is $P(V_{\mathrm{m}} - b) = RT$, and let us find out an expression for the fugacity, f, of this gas. Thus, for the given gas, $V_{\mathrm{m}} = b + (RT/P)$. Hence,

$$Z = \frac{PV_{\mathrm{m}}}{RT} = \frac{P}{RT}\left(b + \frac{RT}{P}\right) = 1 + b\frac{P}{RT} \Rightarrow Z - 1 = b\frac{P}{RT}$$

Therefore, we have,

$$Z - 1 = b\frac{P}{RT}$$

and

$$\ln\left(\frac{f}{P}\right) = \int_0^P \frac{Z-1}{P}\,dP = \int_0^P \frac{1}{P}b\frac{P}{RT}\,dP = \frac{bP}{RT} \Rightarrow \frac{f}{P} = \exp\left(\frac{bP}{RT}\right)$$

If bP/RT is small, we may write,

$$\frac{f}{P} = \exp\left(\frac{bP}{RT}\right) = 1 + \frac{bP}{RT} + \frac{1}{2!}\left(\frac{bP}{RT}\right)^2 + \frac{1}{3!}\left(\frac{bP}{RT}\right)^3 + \cdots \approx 1 + \frac{bP}{RT} = \frac{RT + bP}{RT}$$

From the given equation of state, we have, $RT + bP = PV_{\mathrm{m}}$, and hence,

$$\frac{f}{P} = P\left(\frac{V_{\mathrm{m}}}{RT}\right) = \frac{P}{P_{\mathrm{ideal}}}$$

Therefore,

$$P^2 = fP_{\mathrm{ideal}} \Rightarrow P = \sqrt{fP_{\mathrm{ideal}}}$$

That is, the pressure of the gas is the geometric mean of the ideal pressure and fugacity. [Recall that the geometric mean, GM of n numbers, $a_1,\ a_2,\ a_3,\ \cdots,\ a_n$ is $GM = \sqrt[n]{a_1 \cdot a_2 \cdot a_3 \cdot \cdots \cdot a_n}$]

Example 2

Given a situation where we have an expression for the fugacity, f, of a certain real gas. Say, it is given that,

$$f = P + \alpha P^2,$$

where α is a function of T only, that is, $\alpha = \alpha(T)$. Can we find out the equation of state for the gas? Yes, we can, and let us do it. Given that,

$$f = P + \alpha P^2 \Rightarrow \frac{f}{P} = 1 + \alpha P \Rightarrow \ln\frac{f}{P} = \ln(1 + \alpha P)$$

Since,

$$\ln\left(\frac{f}{P}\right) = \int_0^P \frac{Z-1}{P}\,dP \text{ ,we have, } \ln(1 + \alpha P) = \int_0^P \frac{Z-1}{P}\,dP$$

Now,

$$\ln(1 + \alpha P) = \int_0^P \frac{\alpha}{1 + \alpha P}\,dP \text{, so that, } \int_0^P \frac{\alpha}{1 + \alpha P}\,dP = \int_0^P \frac{Z-1}{P}\,dP$$
$$\therefore \frac{\alpha}{1 + \alpha P} = \frac{Z-1}{P}$$

From,

$$\frac{\alpha}{1 + \alpha P} = \frac{Z-1}{P}$$

we rewrite as,

$$\frac{\alpha}{1+\alpha P} = \frac{\left(V_{\mathrm{m}}/V_{\mathrm{m,\,ideal}}\right)-1}{P} = \frac{\left(V_{\mathrm{m}}P/RT\right)-1}{P}$$

Therefore,

$$\frac{PV_{\mathrm{m}}}{RT} = 1 + \frac{\alpha P}{1+\alpha P}$$

is the desired equation of state for the gas whose fugacity is given by $f = P + \alpha P^2$.

Thermodynamics of Solutions: The Concept of Ideal Solutions

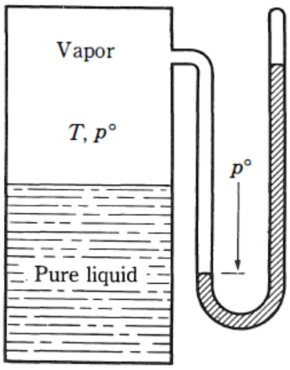
A solution is a homogeneous mixture of chemical species dispersed on a molecular scale. By this definition, a solution is a single phase. A solution may be gaseous, liquid, or solid. Binary solutions are composed of two constituents, ternary solutions three, quaternary four. The constituent present in the greatest amount is ordinarily called the solvent, while those constituents – one or more – present in relatively small amounts are called the solutes. The distinction between solvent and solute is an arbitrary one. We shall employ the words solvent and solute in the ordinary way, realizing that nothing fundamental distinguishes them.

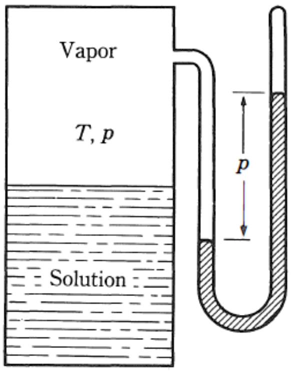
Types of solution:

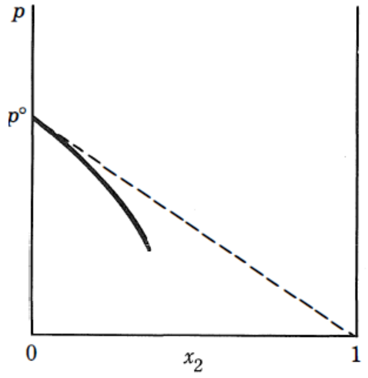
- Gaseous solutions: Mixtures of gases or vapors
- Liquid solutions: Solids, liquids, or gases, dissolved in liquids
- Solid solutions:
  Gases dissolved in solids: H_2 in palladium, N_2 in titanium
  Liquids dissolved in solids: Mercury in gold
  Solids dissolved in solids: Copper in gold, zinc in copper (brasses)

The ideal gas law is an important example of a limiting law. As the pressure approaches zero, the behavior of any real gas approaches that of the ideal gas as a limit. Thus, all real gases behave ideally at zero pressure, and for practical purposes they are ideal at low finite pressures. From this generalization of experimental behavior, the ideal gas is defined as one that behaves ideally at any pressure. We arrive at a similar limiting law from observing the behavior of solutions.

For simplicity, we consider a solution composed of a volatile solvent and one or more involatile solutes, and examine the equilibrium between the solution and the vapor. If a pure liquid is placed in a container that is initially evacuated, the liquid evaporates until the space above the liquid is filled with vapor. The temperature of the system is kept constant. At equilibrium, the pressure established in the vapor is $p°$, the vapor pressure of the pure liquid. If an involatile material is dissolved in the liquid, the equilibrium vapor pressure p over the solution is observed to be less than over the pure liquid.







Since the solute is involatile, the vapor consists of pure solvent. As more involatile material is added, the pressure in the vapor phase decreases. A schematic plot of the vapor pressure of the solvent against the mole fraction of the involatile solute in the solution, x_2 is shown on the right. At $x_2 = 0$, $p = p°$; as x_2 increases, p decreases.

The important feature of the plot is that the vapor pressure of the dilute solution (x_2 near zero) approaches the dashed line connecting $p°$ and zero. Depending on the particular combination of solvent and solute, the experimental vapor-pressure curve at higher concentrations of solute may fall below the dashed line, or above it, or even lie exactly on it. However, for all solutions the experimental curve is tangent to the dashed line at $x_2 = 0$, and approaches the dashed line very closely as the solution becomes more and more dilute.

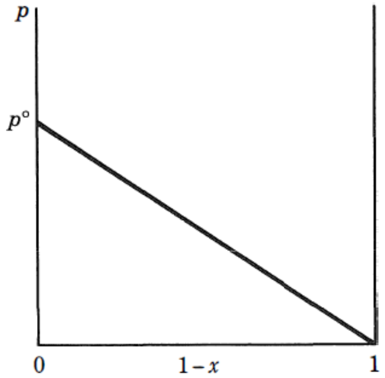
The equation of the ideal (dashed) line is

$$p = p^\circ - p^\circ x_2 = p^\circ(1 - x_2)$$

If x is the mole fraction of solvent in the solution, then $x + x_2 = 1$, and the equation becomes,

$$p = xp^\circ$$

which is **Raoult's law**. It states that the vapor pressure of the solvent over a solution is equal to the vapor pressure of the pure solvent multiplied by the mole fraction of the solvent in the solution. Raoult's law is another example of a limiting law. Real solutions follow Raoult's law more closely as the solution becomes more dilute. The ideal solution is defined as one that follows Raoult's law over the entire range of concentrations. All real solutions behave ideally as the concentration of the solutes approaches zero.



From $p = xp^\circ$, the vapor pressure lowering, $p^\circ - p$, can be calculated,

$$p^\circ - p = p^\circ - xp^\circ = (1 - x)p^\circ \Rightarrow p^\circ - p = x_2 p^\circ$$

The vapor pressure lowering is proportional to the mole fraction of the solute. If several solutes, 2,3, ..., are present, then it is still true that $p = xp^\circ$; but, in this case, $1 - x = x_2 + x_3 + \cdots$ and

$$p^\circ - p = (x_2 + x_3 + \cdots)p^\circ.$$

In a solution containing several involatile solutes, the vapor pressure lowering depends on the sum of the mole fractions of the various solutes. Note particularly that it does not depend on the kinds of solutes present, except that they be involatile. The vapor pressure depends only on the relative numbers of solute molecules. As a generalization of the behavior of real solutions the ideal solution follows Raoult's law over the entire range of concentration. Taking this definition of an ideal liquid solution and combining it with the general equilibrium condition leads to the analytical expression of the chemical potential of the solvent in an ideal solution. If the solution is in equilibrium with vapor, the requirement of the second law is that the chemical potential of the solvent have the same value in the solution as in the vapor, or

$$\mu_{liq} = \mu_{vap}$$

where μ_{liq} is the chemical potential of the solvent in the liquid phase, μ_{vap} the chemical potential of the solvent in the vapor. Since the vapor is pure solvent under a pressure p, the expression for μ_{vap} is given by $\mu_{vap} = \mu_{vap}^\circ + RT\ln p$. Then,

$$\mu_{liq} = \mu_{vap}^\circ + RT\ln p$$

Using Raoult's law, $p = xp^\circ$, in this equation and expanding the logarithm, we obtain

$$\mu_{liq} = \mu_{vap}^\circ + RT\ln p^\circ + RT\ln x$$

If pure solvent were in equilibrium with vapor, the pressure would be p° ; the equilibrium condition is

$$\mu_{liq}^\circ = \mu_{vap}^\circ + RT\ln p^\circ$$

where μ_{liq}° signifies the chemical potential of the pure liquid solvent. Subtracting this equation from the preceding one, we obtain $\mu_{liq} = \mu_{liq}^\circ + RT\ln x$. In this equation, nothing pertaining to the vapor phase appears; omitting the subscript liq, the equation becomes

$$\mu = \mu^\circ + RT\ln x$$

μ is the chemical potential of the solvent in the solution, μ° is the chemical potential of the pure liquid solvent, a function of T and p, and x is the mole fraction of solvent in the solution.