MME 2010
METALLURGICAL THERMODYNAMICS II

Systems of Variable Composition:

Ideal Behavior

Fundamental Property Relation for Systems of Variable Composition

$$d(nG) = (nV)dP - (nS)dT$$

Basic relation connecting the Gibbs free energy to the temperature and pressure of any closed system

For the case of an <u>open system</u>, nG is still a function of T and P, and also a function of the number of moles of each chemical species since material may be taken from or added to the system

$$nG = g(P, T, n_1, , n_2, , n_3, \ldots n_i)$$

differentiating:

$$d(nG) = \underbrace{\left[\frac{\delta(nG)}{\delta P}\right]}_{(nV)}{}_{T,n} dP + \underbrace{\left[\frac{\delta(nG)}{\delta T}\right]}_{-(nS)}{}_{P,n} dT + \sum_i \underbrace{\left[\frac{\delta(nG)}{\delta n_i}\right]}_{(\mu_i)}{}_{P,T,n_j} dn_i$$

$$d(nG) = (nV)dP - (nS)dT + \sum \mu_i dn_i$$

Consider a closed system consisting of two phases that are considered open systems

$$d(nG)^{\alpha} = (nV)^{\alpha} dP - (nS)^{\alpha} dT + \sum \mu_i{}^{\alpha}\, dn_i{}^{\alpha}$$

$$d(nG)^{\beta} = (nV)^{\beta} dP - (nS)^{\beta} dT + \sum \mu_i{}^{\beta}\, dn_i{}^{\beta}$$

A total-system property is expressed by an equation of the following form:

$$nM = (nM)^{\alpha} + (nM)^{\beta}$$

so $$d(nG) = (nV)dP - (nS)dT + \sum \mu_i{}^{\alpha}\, dn_i{}^{\alpha} + \sum \mu_i{}^{\beta}\, dn_i{}^{\beta}$$

Since the two-phase system is closed the constant composition form also holds

$$d(nG) = (nV)dP - (nS)dT$$

Thus at equilibrium $$\sum \mu_i{}^{\alpha}\, dn_i{}^{\alpha} + \sum \mu_i{}^{\beta}\, dn_i{}^{\beta} = 0$$

The changes $dn_i{}^{\alpha}$ and $dn_i{}^{\beta}$ result from mass transfer between phases so that

$$dn_i{}^{\alpha} = -dn_i{}^{\beta}$$

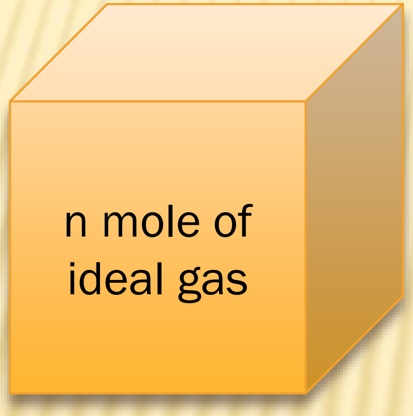
$$\sum (\mu_i{}^{\alpha} - \mu_i{}^{\beta}) dn_i{}^{\alpha} = 0$$

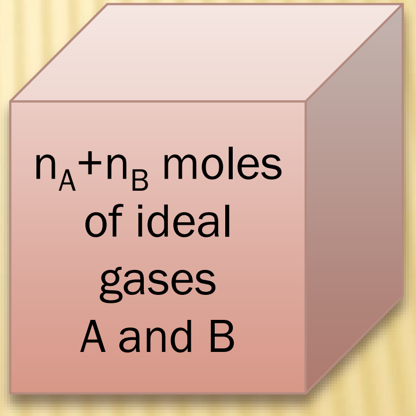
Thus multiple phases at the same T and P are in equilibrium when the chemical potential of each species is the same for all phases

$$\mu_i{}^{\alpha} = \mu_i{}^{\beta} = \cdots = \mu_i{}^{\pi} \qquad (i = 1,2,\ldots,N)$$

The general criteria for equilibrium is applied to systems with given volumetric data according to the relationships between Gibbs energy, enthalpy, entropy, etc.

Let's consider the ideal-gas mixture as the model system





n moles of ideal gas occupies a total volume V' at temperature T

The pressure is

n_A moles of species A in an ideal gas mixture occupy the same volume

$$P = \frac{nRT}{V'} \longrightarrow \frac{p_A}{P} = \frac{n_A}{n} = y_A \longleftarrow p_A = \frac{n_A RT}{V'}$$

$$p_A = y_A P$$

where y_A is the mole fraction of ideal gas A in the gas mixture, and p_A is the *partial pressure* of A. The sum of the partial pressures equals the total pressure

Gibbs' Theorem states that:

A total thermodynamic property such as nG, nS, nV, etc. of an ideal gas mixture is the sum of the total properties of the individual species, each evaluated at the mixture temperature but at its own partial pressure

Mathematical expression for the general property M is as follows:

$$nM^{ig}(T,P) = \sum n_i M^{ig}{}_i(T,p_i)$$

$$M^{ig}(T,P) = \sum y_i M^{ig}{}_i(T,p_i) \qquad (i = 1,2,\ldots,N)$$

Exceptions are enthalpy and internal energy of ideal gas which are independent of pressure

$$\boxed{H^{ig}(T,P) = \sum y_i H^{ig}{}_i(T,P)}$$

$$\boxed{U^{ig}(T,P) = \sum y_i U^{ig}{}_i(T,P)}$$

since

$$dH = C_P dT + \left[V - T\left(\frac{\delta V}{\delta T}\right)_P\right] dP$$

$$(dH = TdS + VdP)$$

$$dU^{ig} = C_V dT$$

The entropy of an ideal gas depends on pressure since

$$dS = C_p \frac{dT}{T} - \left(\frac{\delta V}{\delta T}\right)_P dP \qquad \text{and} \qquad dS^{ig} = C_p{}^{ig} \frac{dT}{T} - \frac{R}{P} dP$$

At constant temperature $dS^{ig}{}_i = -Rd \ln P$

$$S^{ig}{}_i(T,P) - S^{ig}{}_i(T,p_i) = -R \ln \frac{P}{p_i} = -R \ln \frac{P}{y_i P} = R \ln y_i$$

rearranging gives $S^{ig}{}_i(T,p_i) = S^{ig}{}_i(T,P) - R \ln y_i$

since total entropy is

$$S^{ig}(T,P) = \sum y_i S^{ig}{}_i(T,p_i) = \sum (S^{ig}{}_i(T,P) - R \ln y_i \ )$$

$$\boxed{S^{ig}(T,P) = \sum y_i S^{ig}{}_i(T,P) - R \sum y_i \ln y_i}$$

Total entropy of the ideal gas mixture

This general relation applies for the Gibbs free energy of ideal gas mixture,

$$G^{ig} = H^{ig} - TS^{ig}$$

substituting with the enthalpy and entropy terms gives,

$$G^{ig}(T,P) = \underbrace{\sum y_i H^{ig}{}_i(T,P) - T\sum y_i S^{ig}{}_i(T,P)}_{\sum y_i G^{ig}{}_i(T,P)} + RT\sum y_i \ln y_i$$

hence,

$$\boxed{G^{ig}(T,P) = \sum y_i G^{ig}{}_i\,(T,P) + RT\sum y_i \ln y_i}$$

where G^{ig} is the total Gibbs free energy of the ideal gas mixture at the mixture temperature and pressure

Effect of Mixing

When appropriate amounts of a pure species at T and P are mixed to form one mole of mixture at the same T and P, a change in thermodynamic properties occurs

$$M - \sum y_i M_i = change\ of\ M\ by\ mixing$$

Enthalpy change of mixing is zero for ideal gases:

$$H^{ig} - \sum y_i H^{ig}{}_i = 0$$

Entropy change of mixing is always positive since mixing processes are irreversible:

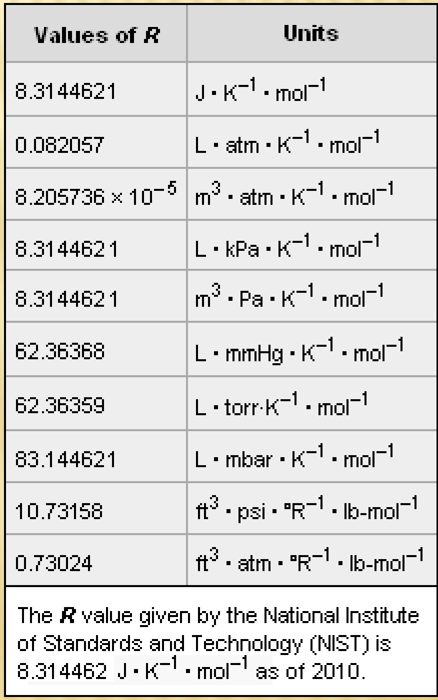
$$S^{ig} - \sum y_i S^{ig}{}_i = R \sum y_i \ln \frac{1}{y_i}$$

Change in Gibbs free energy by mixing is always negative and proportional to the entropy change in quantity

$$G^{ig} - \sum y_i G^{ig}{}_i = RT \sum y_i \ln y_i$$

Example – What is the change in entropy when 0.7 m^3 of CO_2 and 0.3 m^3 of N_2 blend to form a homogeneous gas mixture at 1 bar and 25 °C if they can be considered ideal gases?

Example – A vessel divided into two parts by a partition contains 4 mol of nitrogen gas at 75 C and 30 bar on one side and 2.5 mol of argon gas at 130 C and 20 bar on the other. What is the change in entropy if partition is removed and the gases mix adiabatically and completely? N_2 and Ar are considered ideal gases with C_v=5/2R and 3/2R respectively



Values of *R*	Units
8.3144621	$J \cdot K^{-1} \cdot mol^{-1}$
0.082057	$L \cdot atm \cdot K^{-1} \cdot mol^{-1}$
8.205736×10^{-5}	$m^3 \cdot atm \cdot K^{-1} \cdot mol^{-1}$
8.3144621	$L \cdot kPa \cdot K^{-1} \cdot mol^{-1}$
8.3144621	$m^3 \cdot Pa \cdot K^{-1} \cdot mol^{-1}$
62.36368	$L \cdot mmHg \cdot K^{-1} \cdot mol^{-1}$
62.36359	$L \cdot torr \cdot K^{-1} \cdot mol^{-1}$
83.144621	$L \cdot mbar \cdot K^{-1} \cdot mol^{-1}$
10.73158	$ft^3 \cdot psi \cdot °R^{-1} \cdot lb\text{-}mol^{-1}$
0.73024	$ft^3 \cdot atm \cdot °R^{-1} \cdot lb\text{-}mol^{-1}$

The ***R*** value given by the National Institute of Standards and Technology (NIST) is 8.314462 $J \cdot K^{-1} \cdot mol^{-1}$ as of 2010.

The Gibbs free energy of n moles of ideal gas mixture :

$$nG^{ig} = \sum n_i G^{ig}{}_i + RT \sum n_i \ln y_i$$

since $y_i = n_i/n$,

$$nG^{ig} = \sum n_i G^{ig}{}_i + RT \sum n_i \ln n_i - RT \sum n_i \ln n$$

and since $\mathrm{n} = \sum n_i$,

$$nG^{ig} = \sum n_i G^{ig}{}_i + RT \sum n_i \ln n_i - RTn \ln n$$

Seperating particular species A from the set $\{i\}$ of all species, set $\{j\}$ of all species except A is left in the equation:

$$nG^{ig} = n_A G^{ig}{}_A + \sum n_j G^{ig}{}_j + RTn_A \ln n_A + RT \sum n_j \ln n_j - RTn \ln n$$

The chemical potential of species *A* in an ideal gas mixture:

$$\mu_A{}^{ig} = \left[\frac{\delta(nG)}{\delta n_A}\right]_{P,T,n_j}$$

and the Gibbs free energy:

$$nG^{ig} = n_A G^{ig}{}_A + \sum n_j G^{ig}{}_j + RTn_A \ln n_A + RT\sum n_j \ln n_j - RTn \ln n$$

Gibbs free energies $G^{ig}{}_A$and $G^{ig}{}_j$ are constant since the differentiation is at constant temperature, pressure and composition of species other than A

Therefore

$$\mu_A{}^{ig} = G^{ig}{}_A + \mathrm{RT}\left[n_A\left(\frac{\delta \ln n_A}{\delta n_A}\right)_j + \ln n_A\right] - RT\left[n\left(\frac{\delta \ln n}{\delta n_A}\right)_j + \ln n\left(\frac{\delta n}{\delta n_A}\right)_j\right]$$

Since $n = n_A + \sum n_j$, $\left(\frac{\delta n}{\delta n_A}\right)_j = 1$, so the equation reduces to

$$\mu_A{}^{ig} = G_A{}^{ig} + RT\ln\frac{n_A}{n}$$

or

$$\boxed{\mu_A{}^{ig} = G_A{}^{ig} + RT\ln y_A}$$

Ideal Solutions

A liquid mixture comprised of molecules of the same size and equal forces between all molecules is regarded as an ideal solution

Like ideal gas mixtures, total properties of the ideal solution depend only on the properties of the pure species and their concentrations in the solution:

$$V^{id} = \sum x_i V_i$$

where V^{id} is the molar volume of the ideal solution formed from pure species with real molar volumes V_i at the temperature and pressure of the mixture

Formation of ideal solutions results in no change in total volume or molecular energies, hence enthalpy of formation is similar to ideal gas mixtures:

$$H^{id} = \sum x_i H_i$$

The entropy of an ideal solution increases by mixing since it is an irreversible process

$$S^{id} = \sum x_i S_i - R \sum x_i \ln x_i$$

This general relation applies for the Gibbs free energy of ideal solution,

$$G^{id} = H^{id} - TS^{id}$$

substituting with the enthalpy and entropy terms gives,

$$G^{id} = \underbrace{\sum x_i H_i - T\sum x_i S_i}_{\sum x_i G_i} + RT\sum x_i \ln x_i$$

hence,

$$G^{id} = \sum x_i G_i + RT\sum x_i \ln x_i$$

Where the quantities H_i, S_i, G_i are the properties of any pure species i at the mixture temperature and pressure

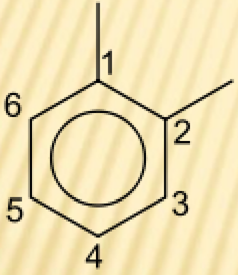
The chemical potential of species A in an ideal solution is again obtained by derivation of Gibbs free energy

$${\mu_A}^{id} = G_A + RT\ln x_A$$

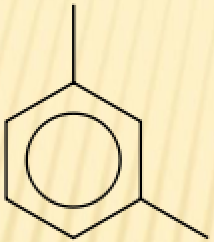
An ideal solution shows thermodynamic mixing characteristics identical to those of ideal gas mixtures except ideal solutions have intermolecular interactions equal to those of the pure components

Behavior of solutions comprised of molecules not too different in size and of the same chamical nature is approximated to ideal solution behavior

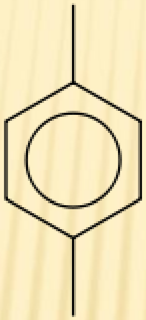
A mixture of isomers conforms closely to ideal solution behavior



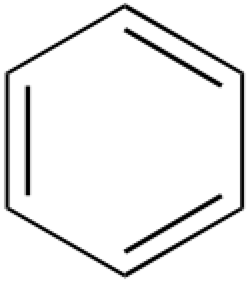
1,2-dimethylbenzene
(*ortho*-xylene)



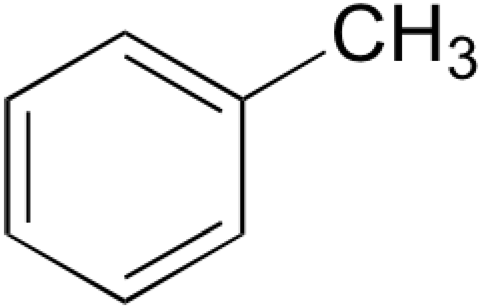
1,3-dimethylbenzene
(*meta*-xylene)



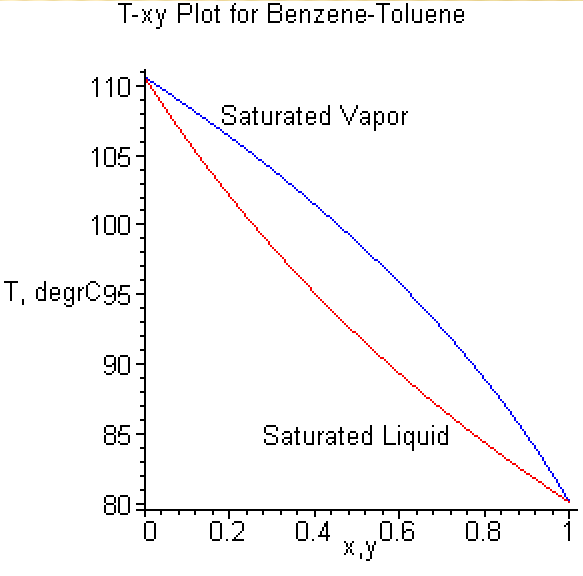
1,4-dimethylbenzene
(*para*-xylene)



benzene



toluene



Example – How many moles of pure methanol and pure water at 25 °C should be mixed to form 2000 cm^3 of antifreeze consisting of 30 mol % methanol in water at 25 °C? Consider antifreeze as a) ideal solution and b) real solution. Molar volumes of pure species and partial molar volumes at 25 °C are given as

V_M= 40.727 cm^3/mol, V_M^P= 38.632 cm^3/mol

V_W= 17.765 cm^3/mol, V_W^P= 18.068 cm^3/mol

Consider a liquid phase and a vapor phase coexisting in equilibrium at T and P

The condition of vapor/liquid equilibrium requires that:

$$\mu_i{}^v = \mu_i{}^l \qquad (i = 1,2,\dots,N)$$

If the vapor phase is approximated by an ideal gas and liquid phase by an ideal solution, the chemical potentials in the equality may be replaced as:

$$G_i{}^{ig} + RT\ln y_i = G_i{}^l + RT\ln x_i$$

rearranging gives

$$RT\ln\frac{y_i}{x_i} = G_i{}^l(T,P) - G_i{}^{ig}(T,P)$$

where pure species properties are evaluated at the equilibrium T and P

Since the extensive properties of liquids have low pressure dependency:

$$G_i{}^l(T,P) \cong G_i{}^l\left(T,P_i{}^{sat}\right)$$

where $P_i{}^{sat}$ is the saturation or vapor pressure of pure species i at temperature T

Gibbs free energy of pure i:

$$dG_i{}^{ig} = V_i{}^{ig}dP - S_i{}^{ig}dT$$

For constant T, the pressure dependence of Gibb free energy is given as

$$dG_i{}^{ig} = V_i{}^{ig}dP$$

integrating,

$$G_i{}^{ig}(T, P_i{}^{sat}) - G_i{}^{ig}(T, P) = \int_P^{P_i{}^{sat}} \frac{RT}{P}dP = RT\ln\frac{P_i{}^{sat}}{P}$$

remember that

$$RT\ln\frac{y_i}{x_i} = G_i{}^{l}(T, P_i{}^{sat}) - G_i{}^{ig}(T, P)$$

substituting: $RT\ln\frac{y_i}{x_i} = G_i{}^{l}(T, P_i{}^{sat}) - G_i{}^{ig}(T, P_i{}^{sat}) + RT\ln\frac{P_i{}^{sat}}{P}$

Gibbs free energies of two phases coexisting at the same T and $P_i{}^{sat}$ are equal

Thus,

Raoult's law

$$\boxed{y_iP = x_iP_i{}^{sat}}$$

The partial pressure of species i in the vapor phase is equal to the product of liquid phase mole fraction of i and its vapor pressure

$$\boxed{y_i P = x_i P_i^{sat}} \qquad (i = 1,2, \dots, N)$$

Raoult's law is a set of *N* equations connecting variables *T, P, y_i*, and *x_i*

T

P

N-1 independent vapor phase mole fractions

N-1 independent liquid phase mole fractions

Total number of independent variables: *2N*

Specification of *N* of these variables allows the remaining *N* variables to be determined by solution of the *N* equilibrium relations given by the Raoult's law

Example – The binary system acetonitrile/nitromethane conforms closely to Raoult's law. Determine the partial pressure of acetonitrile in vapor phase at 75 °C for a liquid composition of x_a=0.6

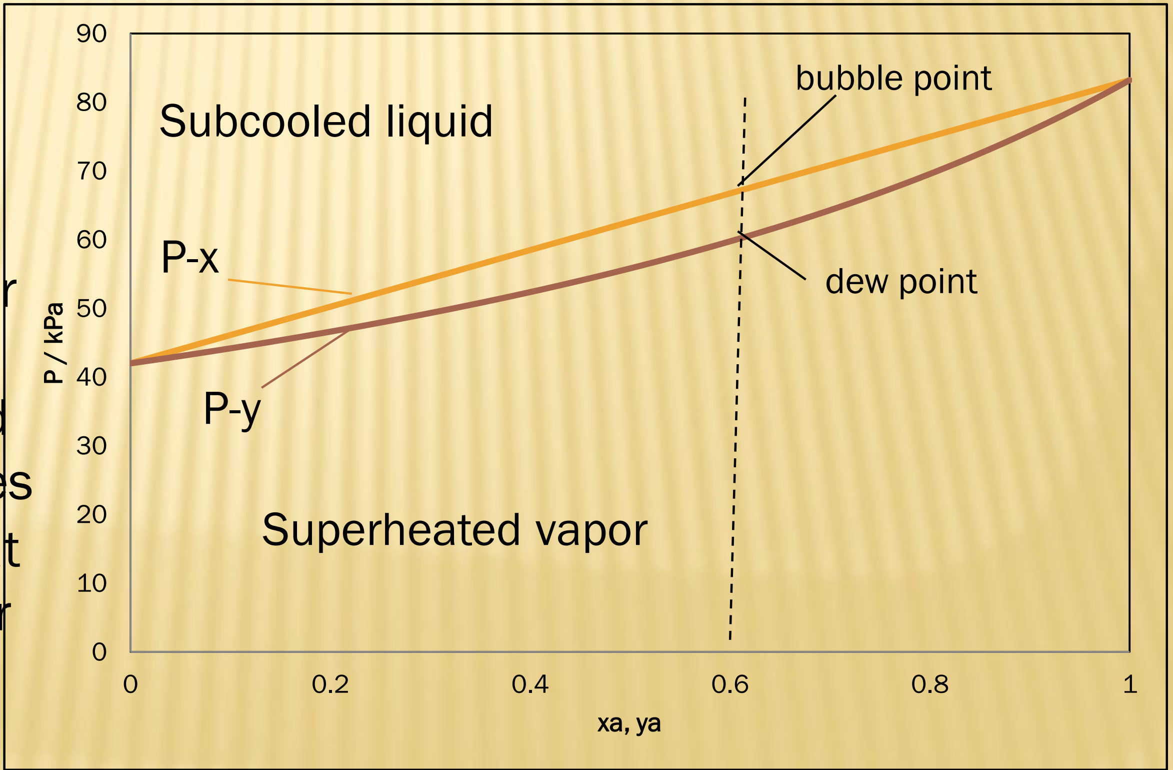
$$\ln P_a^{sat} = 14.27 - \frac{2945.47}{T + 224}$$

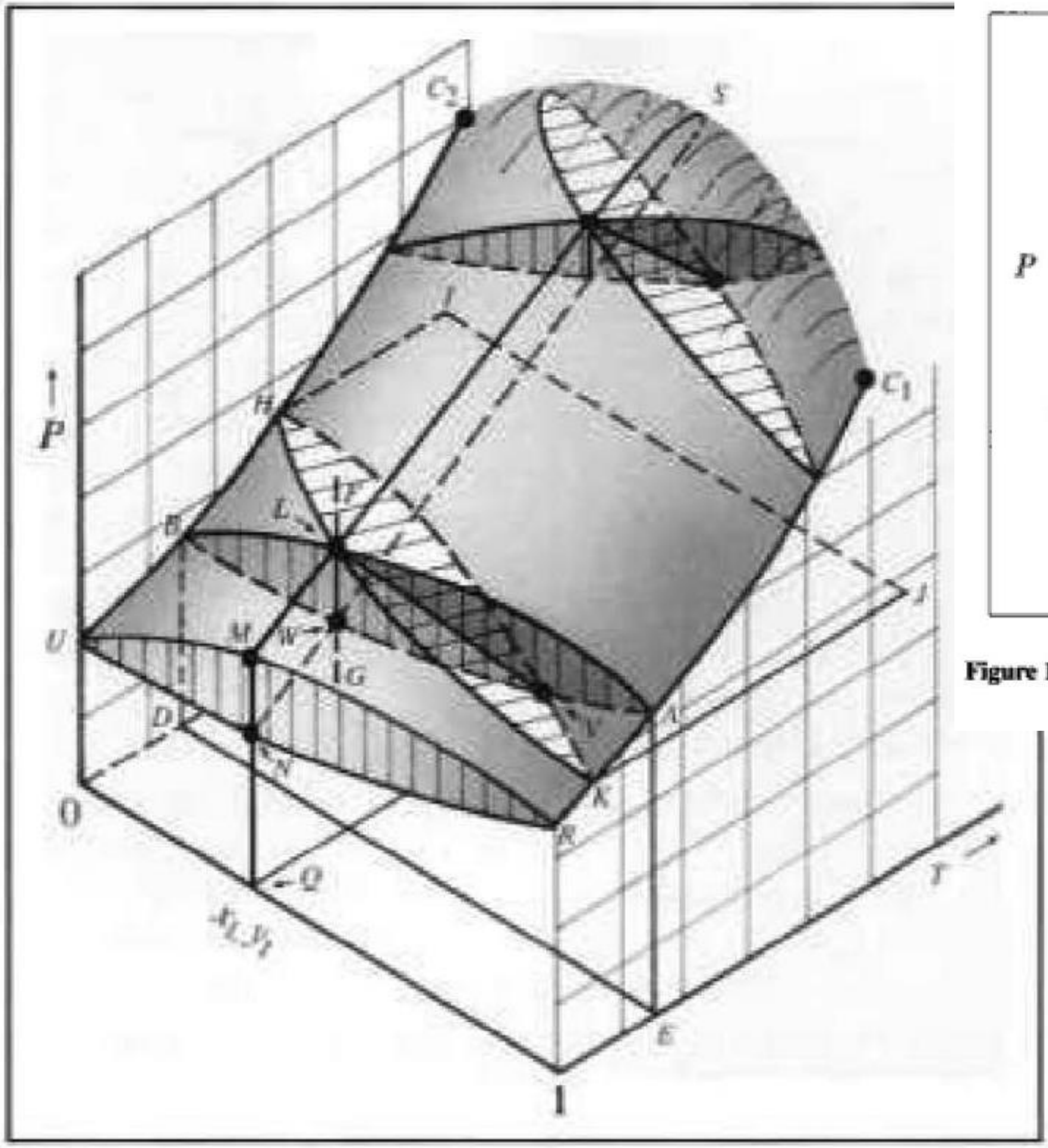
$$\ln P_n^{sat} = 14.20 - \frac{2972.64}{T + 209}$$

A plot of pressures calculated as a function of liquid concentration versus liquid-vapor concentrations gives the vapor/liquid equilibrium pressures in the form of phase diagram

P-x line represents states of saturated liquid
P-y line represents states of saturated vapor
Points between the saturated liquid and saturated vapor lines are in the two-phase region where saturated liquid and saturated vapor coexist in equilibrium
The pressures where P-x and P-y lines intersect at the edges are vapor pressures ${P_a}^{sat}$ and ${P_n}^{sat}$ where saturated liquid and saturated vapor of pure species coexist

When P is fixed, temperature varies along composition axis as an indirect function of vapor pressures
Temperature range is bounded by the saturation temperartures ${T_a}^{sat}, {T_n}^{sat}$ the temperatures at which pure species exert vapor pressures equal to P
T-xy variation can be plotted





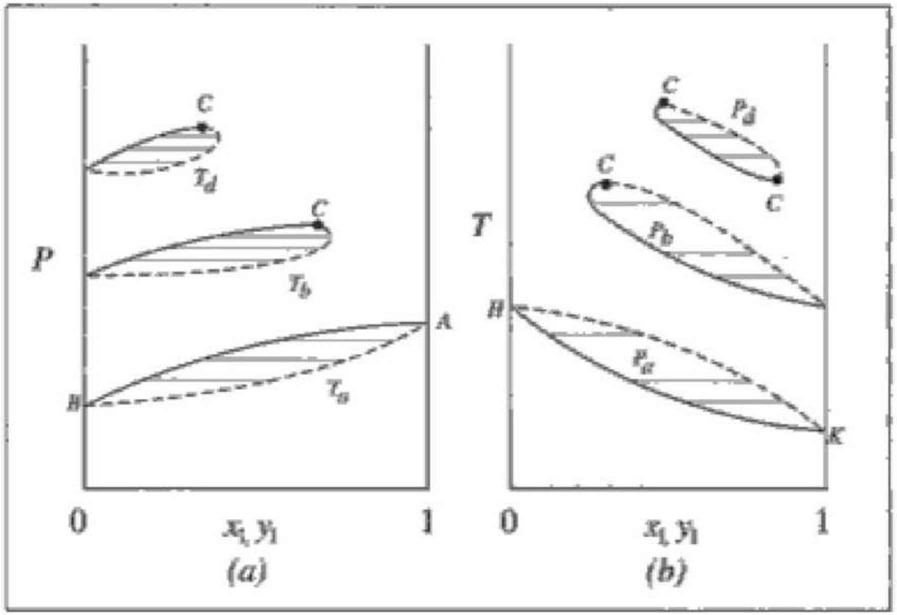
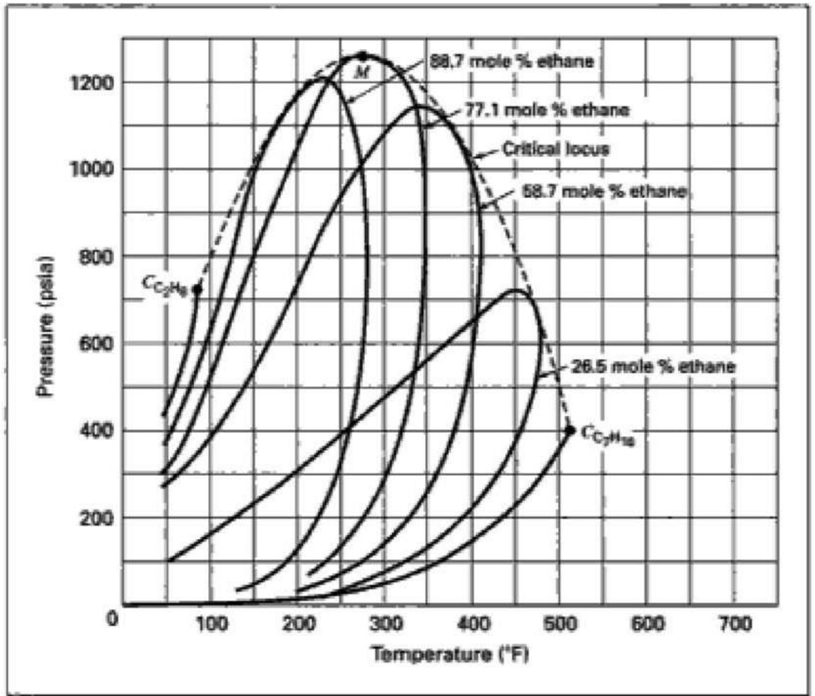


Figure 10.2: (*a*) *Pxy* diagram for three temperatures. (*b*) *Txy* diagram for three pressures.
—— Saturated liquid (bubble line); - - - Saturated vapor (dew line)



Raoult's law is an approximation based on ideal solutions

It is applicable to solvents of dilute solutions for a narrow high concentration range

Partial pressure of solute in dilute non-ideal solutions is related closely by Henry's law:

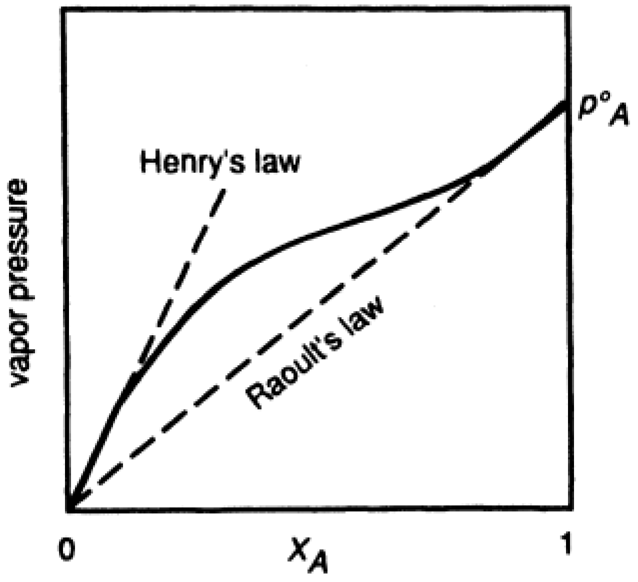
$$P_i = hx_i$$

The proportionality constant h depends on the solute and solvent chemical species

Henry's law becomes Raoult's law when h equals the vapor pressure of pure solvent

Activity is a conversion function relating vapor pressures of condensed phases and non-ideal gases to thermodynamic equations derived for ideal gas mixtures of pure species

$$a_i = \frac{P_i}{P_i{}^o} = \left(\frac{h}{P_i{}^o}\right)x_i = \gamma_{\,i}x_i$$



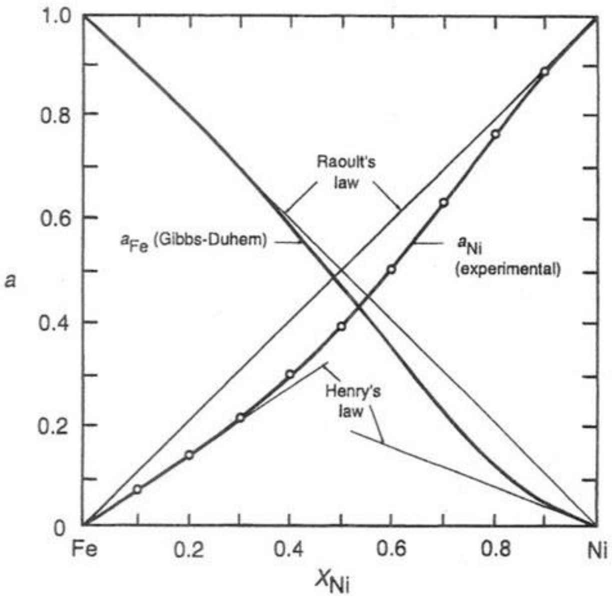


Figure 9.8 Activities in the system iron-nickel at 1600°C. (From G. R. Zellars, S. L. Payne, J. P. Morris, and R. L. Kipp, "The Activities of Iron and Nickel in Liquid Fe-Ni Alloys," *Trans. AIME* (1959), vol. 215, p. 181.)

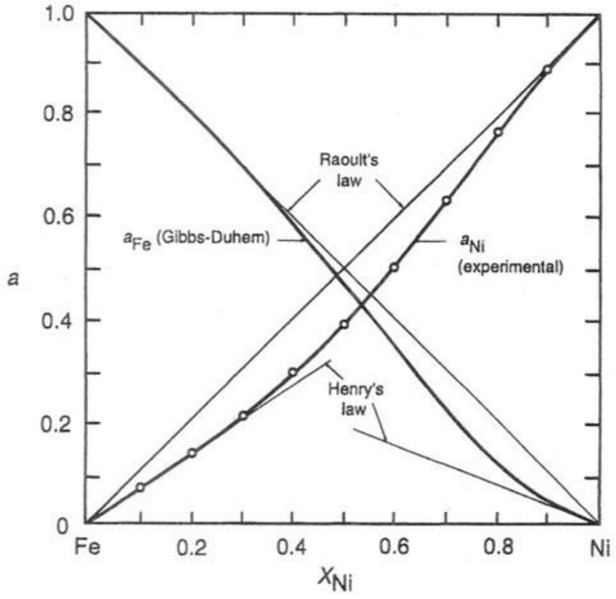
$$a_i = \frac{P_i}{P_i{}^o} = \left(\frac{h}{P_i{}^o}\right) x_i = \gamma_{\ i} x_i$$

Activity of ideal solutions equal the concentration of species so that $\gamma = 1$

Activity coefficient of dilute real solutions that conform to Henry's law may be greater or less than 1

Activity coefficient is function of molecular interactions and hence, mole fractions

For the narrow dilute concentration range where Henry's law is applicable, activity coefficient is constant



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Relation between Raoult's and Henry's law

In a dilute solution, activity of solute B varies according to Henry's law while the activity of solvent A conforms to Raoult's law within the same concentration range

$$a_B = \gamma_B x_B \quad where\ \gamma_B = \frac{h}{P_B{}^o} = constant$$

$$P_A = y_A P = x_A P_A{}^{sat}, \qquad a_A = \frac{P_A}{P_A{}^{sat}} = x_A$$

Derivation follows from partial Gibbs free energy equation:

$$x_A dG_A{}^P + x_B dG_B{}^P = 0$$

$$dG_A{}^P = RTd\ln a$$

$$x_A d\ln a_A + x_B d\ln a_B = 0$$

since $d\ln a_B = d\ln \gamma_B x_B = d\ln x_B$ and $dx_B = x_B d\ln x_B$ and $x_A = 1 - x_B$,
Integrating gives

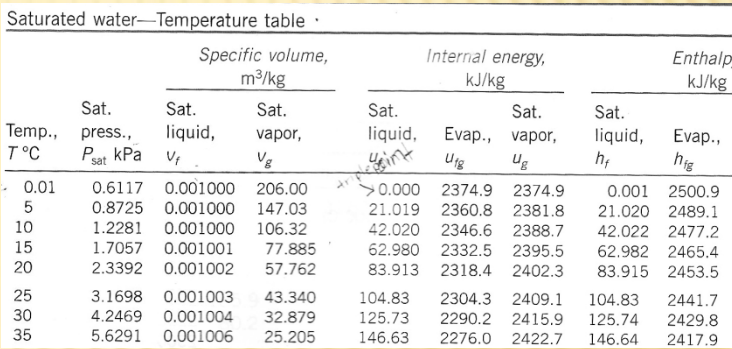
$$\int_{a=1}^{a} d\ln a_A = -\int_0^{x_B} \frac{dx_B}{1 - x_B}$$

$$\ln a = \ln(1 - x_B) = \ln x_A$$

$$a_A = x_A$$

Example – Carbonated water contains CO_2 and H_2O. Determine the composition of the vapor phase in a sealed bottle of soda and the pressure exerted on the bottle at 10 °C if the liquid phase mole fraction of CO_2 is 0.01. Henry's constant for CO_2 in water is about 990 bar.

$$P_H{}^{sat} = 0.01227\ bar$$



Saturated water—Temperature table ·

		Specific volume, m^3/kg		Internal energy, kJ/kg			Enthalp kJ/kg	
Temp., T °C	Sat. press., P_{sat} kPa	Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g	Sat. liquid, h_f	Evap., h_{fg}
0.01	0.6117	0.001000	206.00	0.000	2374.9	2374.9	0.001	2500.9
5	0.8725	0.001000	147.03	21.019	2360.8	2381.8	21.020	2489.1
10	1.2281	0.001000	106.32	42.020	2346.6	2388.7	42.022	2477.2
15	1.7057	0.001001	77.885	62.980	2332.5	2395.5	62.982	2465.4
20	2.3392	0.001002	57.762	83.913	2318.4	2402.3	83.915	2453.5
25	3.1698	0.001003	43.340	104.83	2304.3	2409.1	104.83	2441.7
30	4.2469	0.001004	32.879	125.73	2290.2	2415.9	125.74	2429.8
35	5.6291	0.001006	25.205	146.63	2276.0	2422.7	146.64	2417.9

triple point