MME 2010
METALLURGICAL THERMODYNAMİCS 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 open system, 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

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

differentiating:

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

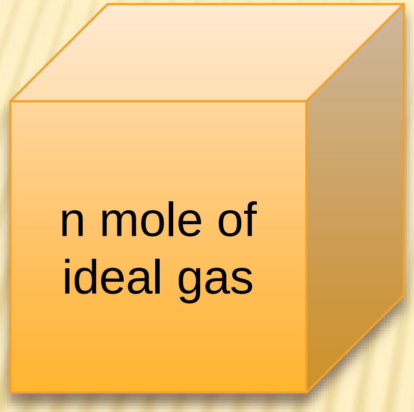
$$d(nG) = (nV)dP - (nS)dT + \sum \mu_i dn_i$$

Consider an ideal-gas mixture as the model system

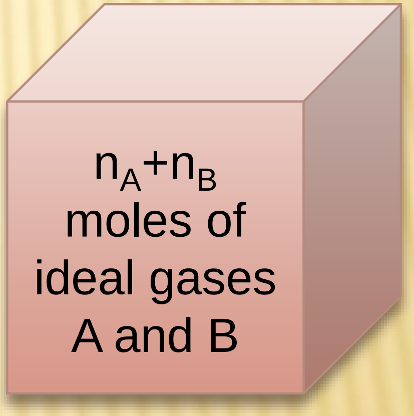
n moles of ideal gas occupies a total volume V' at temperature T

The pressure is

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



n mole of ideal gas



n_A+n_B moles of ideal gases A and B

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

$$p_A = y_A P$$

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

$$\boxed{H^{ig}(T,P) = \sum y_i H^{ig}{}_i(T,P)} \quad \text{since} \quad dH = C_P dT + \left[V - T\left(\frac{\delta V}{\delta T}\right)_P\right] dP$$

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

The entropy of an ideal gas depends on pressure since $dH = TdS + VdP$

$$dS = C_p \frac{dT}{T} - \left(\frac{\delta V}{\delta T}\right)_P dP$$

and

$$dS^{ig} = C_p{}^{ig} \frac{dT}{T} - \frac{R}{P} dP$$

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

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

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

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

Example – What is the entropy of a homogeneous ideal gas mixture of 0.7 m^3 of CO_2 and 0.3 m^3 of N_2 at 1 bar and 25 °C ? $S^o{}_{CO2} = 213\,\frac{J}{K}, S^o{}_{N2} = 192\,\frac{J}{K}$, $\Delta H^o{}_{CO2} = -393510\ J$

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:

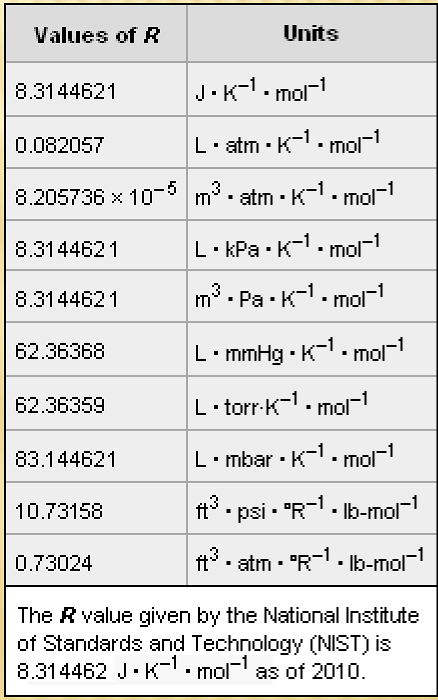
$$S^{ig} - \sum y_i S^{ig}{}_i = R \sum y_i \ln \frac{1}{y_i}$$

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.

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

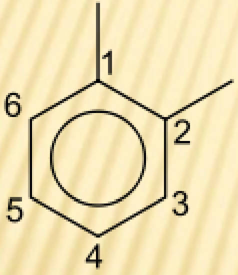
The chemical potential of species A in an ideal solution is again obtained by derivation of Gibbs free energy

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

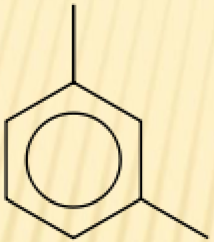
An ideal solution shows thermodynamic mixing characteristics identical to those of ideal gas mixtures except ideal solutions have intermolecular interactions equal to those of the pure components

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

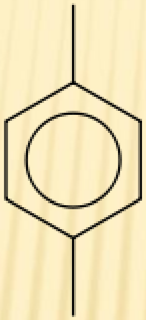
A mixture of isomers conforms closely to ideal solution behavior



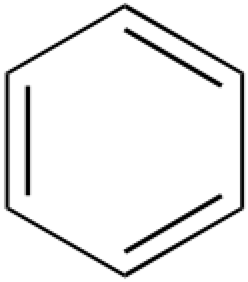
1,2-dimethylbenzene
(*ortho*-xylene)



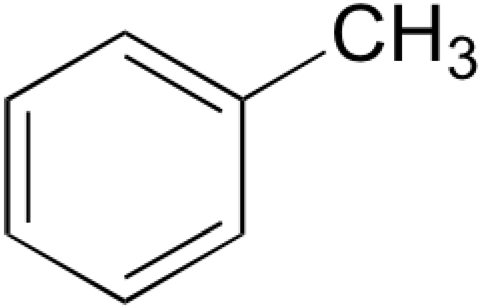
1,3-dimethylbenzene
(*meta*-xylene)



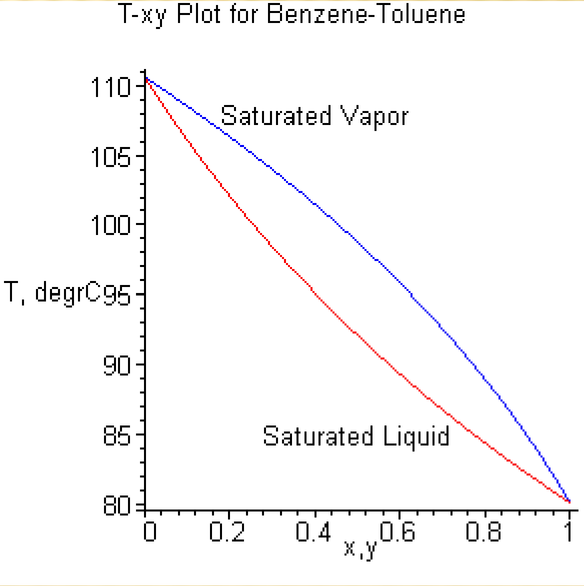
1,4-dimethylbenzene
(*para*-xylene)



benzene



toluene



IDEAL SOLUTİONS EXPLAİNED

https://youtu.be/_x7BHPew2lg

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

MIXING OF REAL SOLUTIONS

https://youtu.be/QNJyyVwzYMY

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

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

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

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

RAOULT'S LAW EXPLAİNED

https://youtu.be/u-xiso3hqBI

Raoult’s law is an approximation based on ideal solutions

$$P_i = P_i^{sat} x_i$$

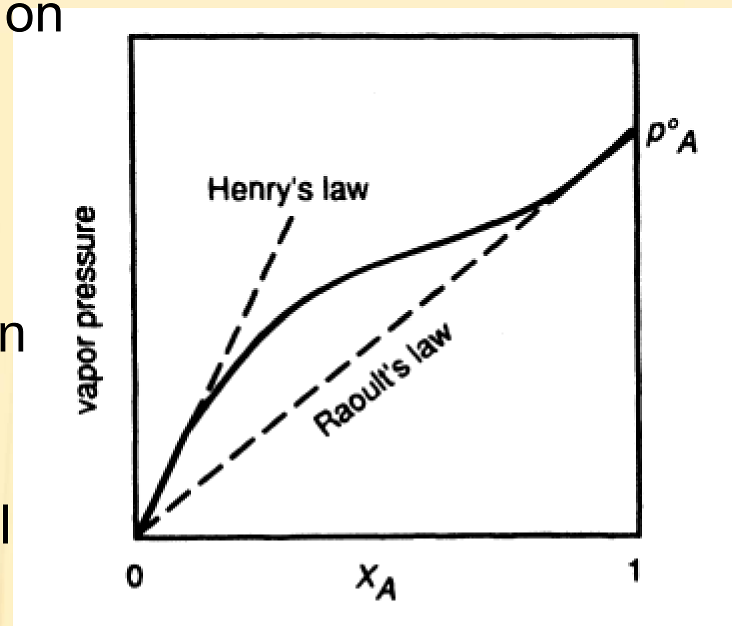
It is applicable to solvents of dilute real solutions for a narrow high concentration range

Partial pressures of solutes in dilute real solutions are related closely by Henry’s law:

$$P_i = h x_i$$

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



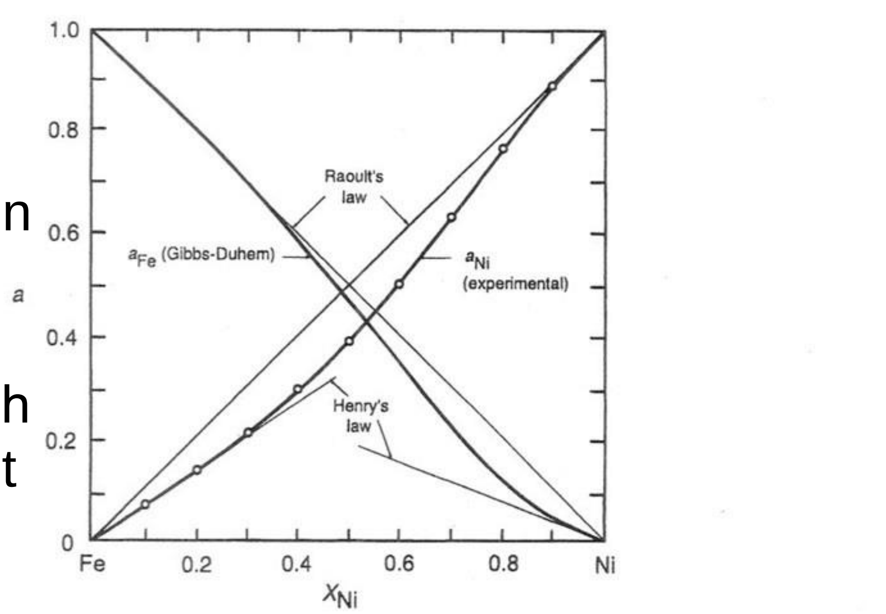
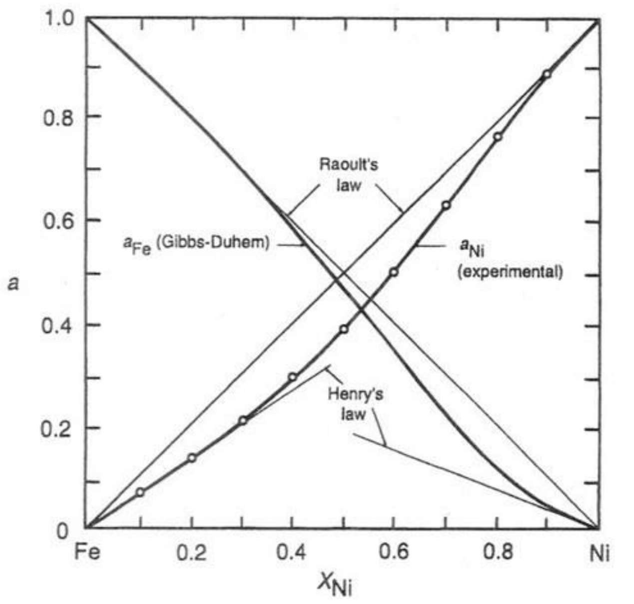


Figure 9.8 Activities in the system iron-nickel at 1600°C. (From G. R. Zellars, S. L. Payne, J. P. Morris, and R. L. Kipp, “The Activities of Iron and Nickel in Liquid Fe-Ni Alloys,” *Trans. AIME* (1959), vol. 215, p. 181.)

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

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



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Activity of ideal solutions equal the concentration of species so that

$$\gamma_{\ i} = \frac{P_i{}^{sat}}{P_i{}^o} = 1, \qquad a_i = x_i$$

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

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:

$$x_A d{G_A}^P + x_B d{G_B}^P = 0$$

since $d{G_A}^P = RTd\ln a$

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

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

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

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

$$a_A = \gamma_B x_A$$

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

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