

# **MME 2010**

# **METALLURGICAL**

# **THERMODYNAMICS II**

Systems of Variable Composition and the

Thermodynamic properties of fluids undergoing phase changes

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## 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:

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

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

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

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



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

$$\mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\pi \quad (i = 1, 2, \dots, N)$$

Chemical potential of a chemical species in a solution is given as:

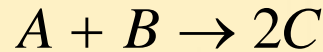
$$\mu_i = G_i + RT \ln a_i$$

Where  $a_i$  is the activity of chemical species  $i$ , which is proportional to its partial pressure  $P_i$

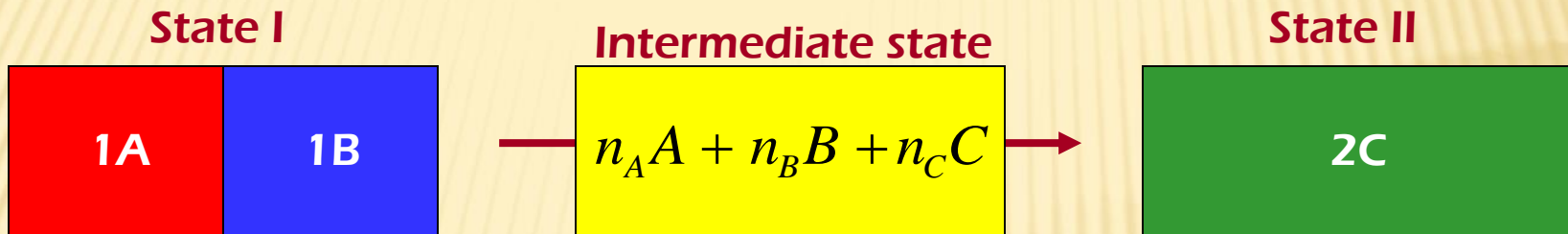
Mole fraction is replaced by activity coefficient in real solutions

Chemical potential is a criteria for equilibrium in phase changing, mixing processes and reacting systems

We considered a simple reaction system as a system of variable composition:



$$\begin{aligned}\Delta G^\circ &= G_{II} - G_I \\ &= 2G_C^\circ - G_A^\circ - G_B^\circ\end{aligned}$$



$$G = n_A \mu_A + n_B \mu_B + n_C \mu_C = n_A \mu_A + n_A \mu_B + 2(1 - n_A) \mu_C$$

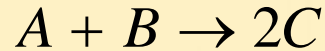
**Recall:**  $\mu_i = G_i^\circ + RT \ln a_i$

$$\begin{aligned}G &= n_A (G_A^\circ + RT \ln a_A) + n_A (G_B^\circ + RT \ln a_B) + 2(1 - n_A) (G_C^\circ + RT \ln a_C) \\ &= n_A G_A^\circ + n_A G_B^\circ + 2(1 - n_A) G_C^\circ + RT [n_A \ln a_A + n_A \ln a_B + 2(1 - n_A) \ln a_C]\end{aligned}$$

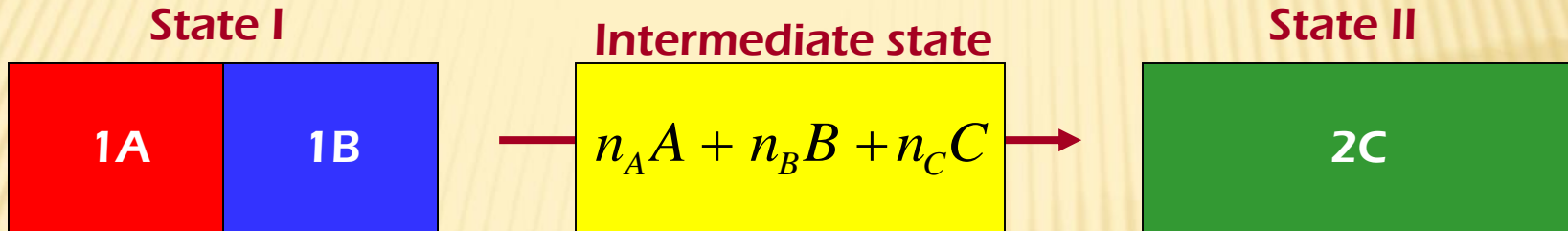
$$\frac{\partial G}{\partial n_A} = \underbrace{G_A^\circ + G_B^\circ - 2G_C^\circ}_{-\Delta G^\circ} + RT (\ln a_A + \ln a_B - 2 \ln a_C) = 0 \quad \text{Equilibrium condition}$$

$$\Delta G^\circ = RT (\ln a_A + \ln a_B - 2 \ln a_C)$$

# Equilibrium condition



$$\begin{aligned}\Delta G^\circ &= G_{II} - G_I \\ &= 2G_C^\circ - G_A^\circ - G_B^\circ\end{aligned}$$



$$\Delta G^\circ = RT(\ln a_A + \ln a_B - 2 \ln a_C)$$

$$\Delta G^\circ = RT \ln \left( \frac{a_A a_B}{a_C^2} \right)$$

$$\Delta G^\circ = -RT \ln \left( \frac{a_C^2}{a_A a_B} \right)$$

$$\Delta G^\circ = -RT \ln K$$

K is defined as an  
"Equilibrium Constant"



## Fluids undergoing phase changes

Volumetric data of substances are needed to calculate the thermodynamic properties such as internal energy and enthalpy, from which the heat and work requirements of processes are obtained

Understanding the P-V-T behavior of pure substances allows the engineer to make accurate estimations to the changes in properties accompanying its state changes

Pressure, volume and temperature are experimentally controllable properties that are connected by equation of state

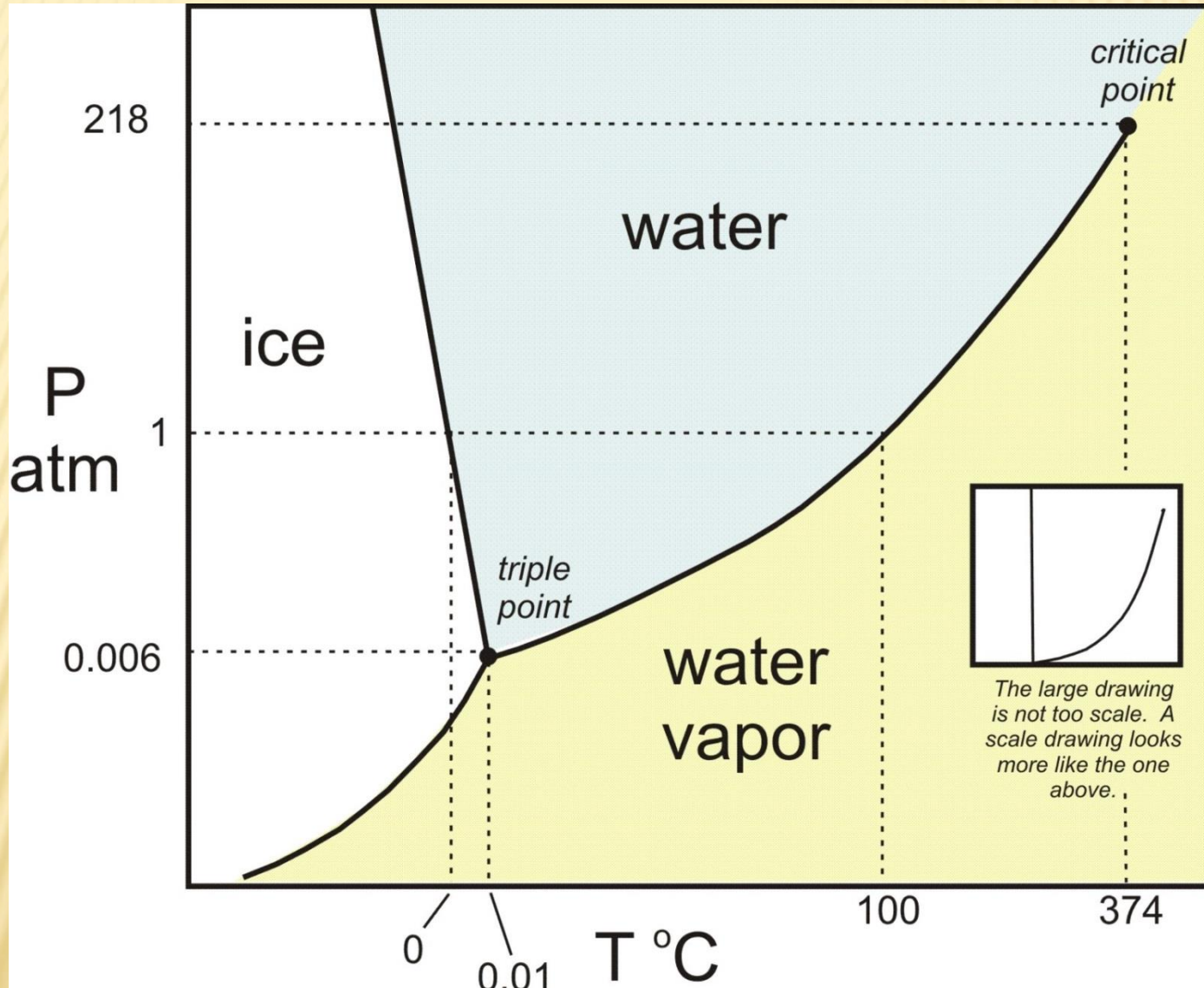
$$V(P, T)$$

$$V = RT/P \quad \text{For ideal gas}$$

A pure substance can have as many as 3 phases coexisting at the same conditions: gas, liquid, solid

P-V-T behavior of any substance can be experimentally obtained and represented in the form of phase diagrams

# Pressure - Temperature diagram of water



It is convenient to call the phase below critical pressure the gas phase and the gas phase below critical temperature the vapor phase which can be condensed to liquid vapor



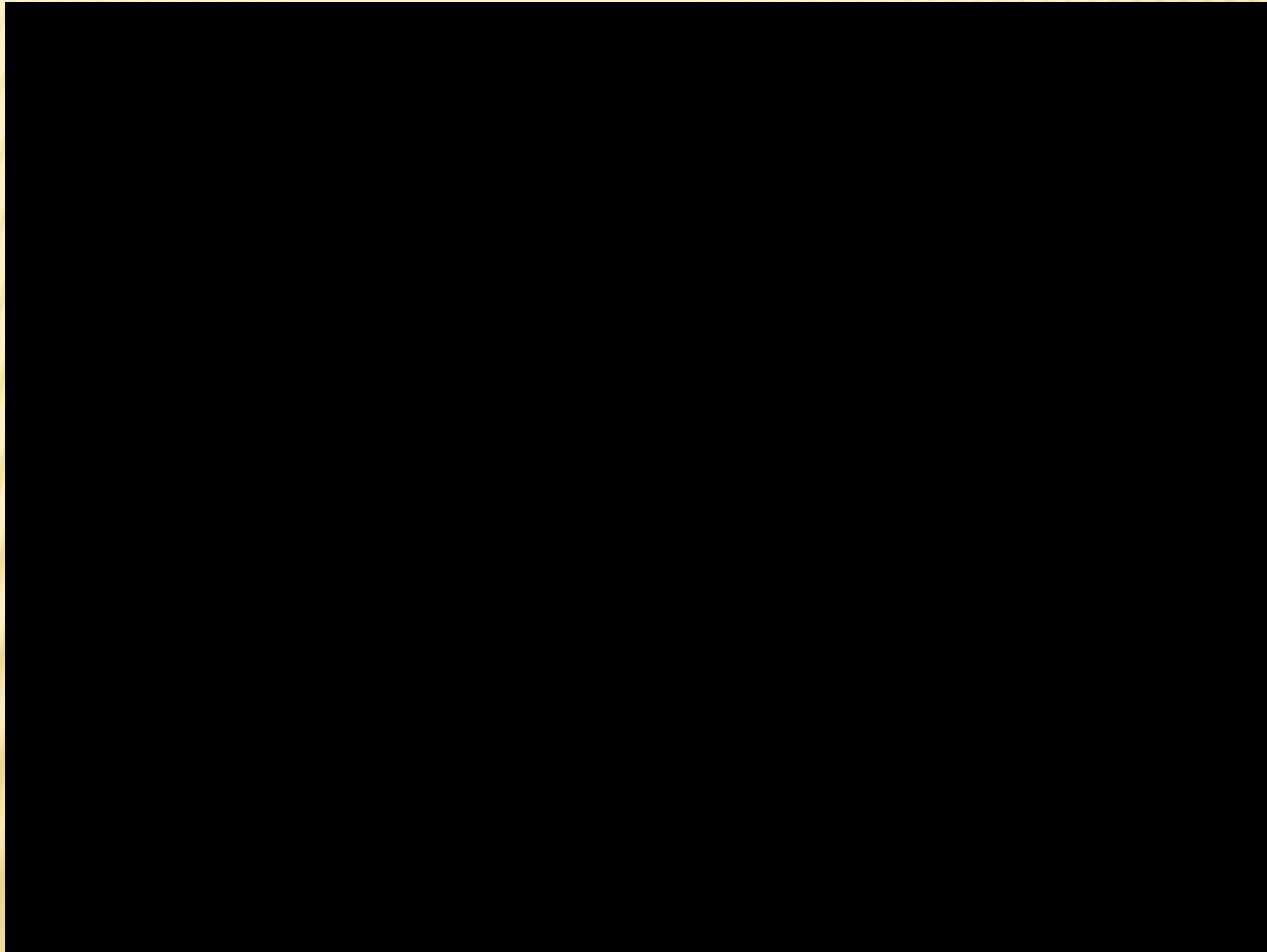
# VAPOR PRESSURE EXPLAINED



[https://youtu.be/re9r0kzQp\\_M](https://youtu.be/re9r0kzQp_M)

# DEMO FOR WATER VAPOR

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[https://youtu.be/i0FrX\\_bPsT8](https://youtu.be/i0FrX_bPsT8)

Abrupt changes in extensive properties such as volume, enthalpy, entropy occur as phases change through the sublimation, fusion and vaporization curves

Gibbs free energy is an exception as it stays constant during a phase change

$$dG = VdP - SdT = 0$$

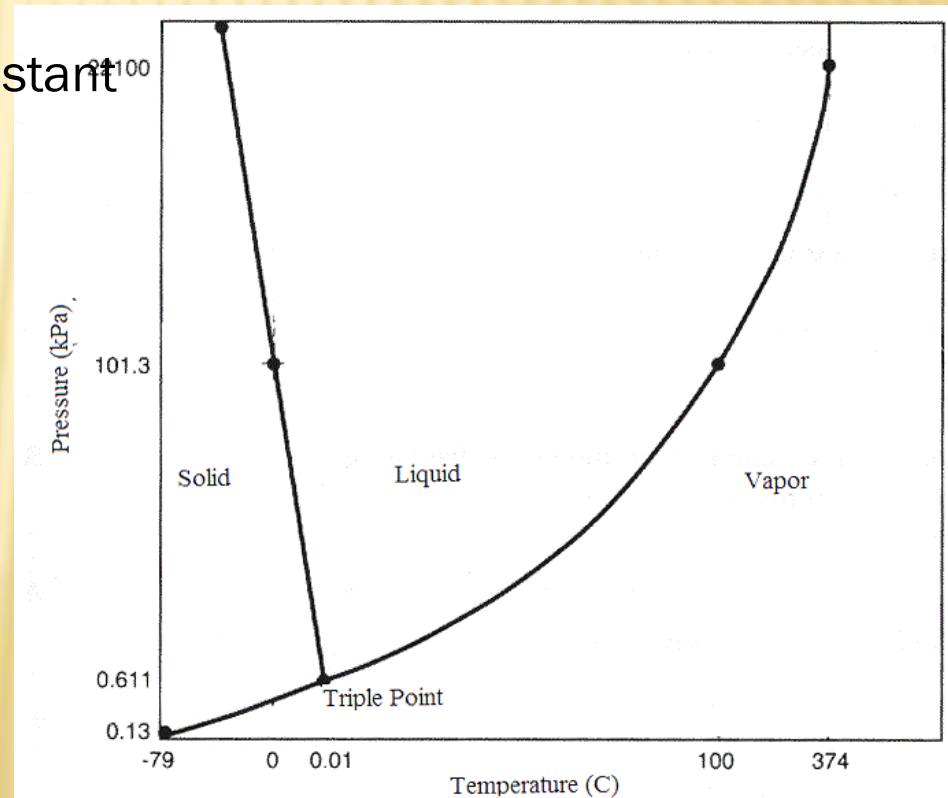
Consider vaporization of water at the boiling point of 100 °C and 101.3 Kpa

Since the phase change occurs at constant T and P,

$$G^l = G^v$$

or more generally

$$G^\alpha = G^\beta$$





Now consider changing the temperature of a two-phase system  
Pressure will also change in accord with the phase rule as the system is univariant

$$dG^{\alpha} = dG^{\beta}$$

$$V^{\alpha} dP^{sat} - S^{\alpha} dT = V^{\beta} dP^{sat} - S^{\beta} dT$$

Rearranging yields

$$\frac{dP^{sat}}{dT} = \frac{S^{\beta} - S^{\alpha}}{V^{\beta} - V^{\alpha}} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}}$$

Hence entropy and volume changes occur when a unit amount of a pure chemical species is transferred from phase  $\alpha$  to phase  $\beta$

Phase change at constant T and P

$$\Delta H^{\alpha\beta} = T\Delta S^{\alpha\beta} \quad (dH = TdS + VdP)$$

substituting above gives

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T_{\alpha\beta}\Delta V^{\alpha\beta}}$$

The equation called Clapeyron equation provides an important connection between properties of different phases and help calculate latent heats of transformation

Example - Lead has a melting temperature of 327 °C at 1 atm. Calculate the melting temperature of lead at 100 atm

Densities of solid and liquid lead = 11.005 g/cm<sup>3</sup>, 10.645 g/cm<sup>3</sup>

Latent heat of melting = 1190 cal/gr

Molecular weight = 207 gr

Clapeyron equation is simplified when the change in temperature during melting, dt, is small compared to T. In this case  $\Delta H$ , T,  $\Delta V$  are nearly constant

$$\Delta T = \left( \frac{T_{\alpha\beta} \Delta V^{\alpha\beta}}{\Delta H^{\alpha\beta}} \right) \Delta P$$

## Calculating latent heat of vaporization at low pressures

Clapeyron equation is simplified in this case by approximating the vapor phase to ideal gas so that the volume of the liquid is negligible compared with the volume of the vapor

$$\Delta V^{lv} = V^v = \frac{RT}{p^{sat}}$$

$$\text{so } \frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}} \longrightarrow \frac{dP^{sat}}{dT} = \frac{\Delta H^{lv}}{RT^2/p^{sat}}$$

rearranging,

$$\frac{dP^{sat}/P^{sat}}{dT/T^2} = \frac{\Delta H^{lv}}{R}$$

or

$$\Delta H^{lv} = -R \frac{d \ln P^{sat}}{d(1/T)}$$

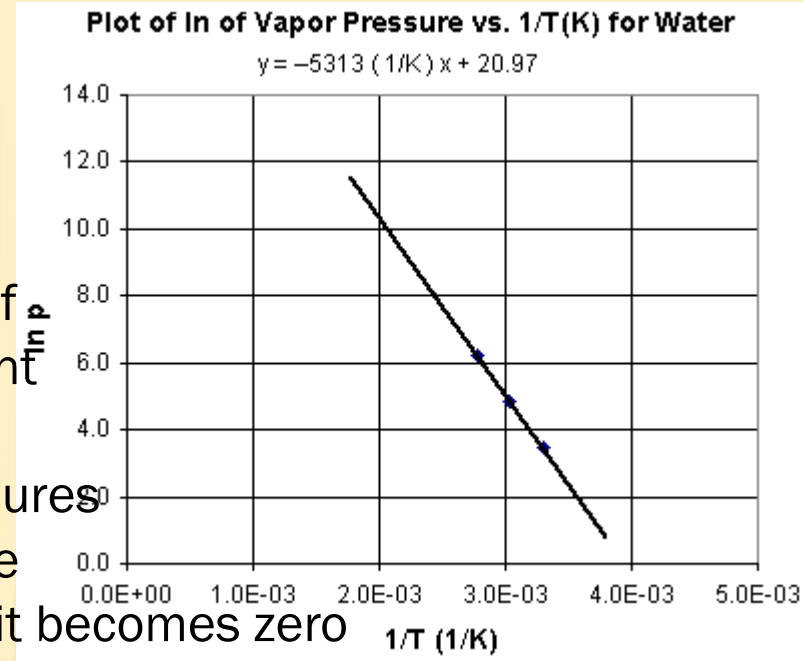
This approximate equation known as the Clausius-Clapeyron eqn. relates the latent heat of vaporization directly to the vapor pressure curve only at low pressures (for ideal gas approximation)



$$\Delta H^{lv} = -R \frac{d \ln P^{sat}}{d(1/T)}$$

Clausius-Clapeyron eqn. implies that the slope of the curve, latent heat of vaporization is constant

This is only true at low temperatures and pressures as  $\Delta H^{lv}$  decreases with increasing temperature from the triple point to the critical point where it becomes zero



More accurate models are present describing the vapor pressure-temperature relationship for the entire temperature range:

$$\ln P^{sat} = A - \frac{B}{T + C} \quad \text{Antoine equation}$$

$$\ln P^{sat} = A - \frac{B}{T} + D \ln T + FT^6 \quad \text{Riedel equation}$$

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

The condition of vapor/liquid equilibrium requires that:

$$\mu_i^v = \mu_i^l \quad (i = 1, 2, \dots, N)$$

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:

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

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 Gibbs 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,

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

Raoult's law

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



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

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  $x_a=0.6$

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

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

# DEMONSTRATION OF RAOULT'S LAW

Raoult's Law for Solution of Two  
Volatile Liquids

flexiguru.com

# RAOULT'S LAW EXPLAINED



<https://youtu.be/u-xiso3hqBl>



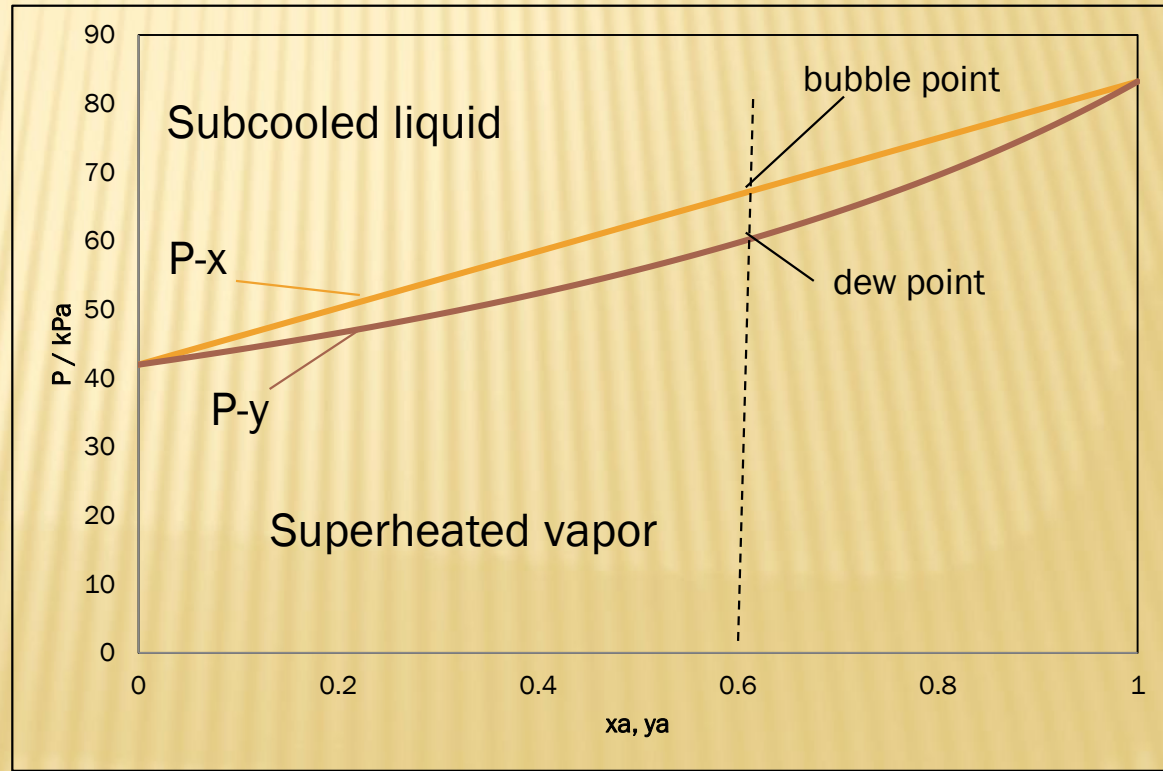
A plot of pressures calculated as a function of liquid-vapor concentrations gives the vapor/liquid equilibrium pressures in the form of phase diagram

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



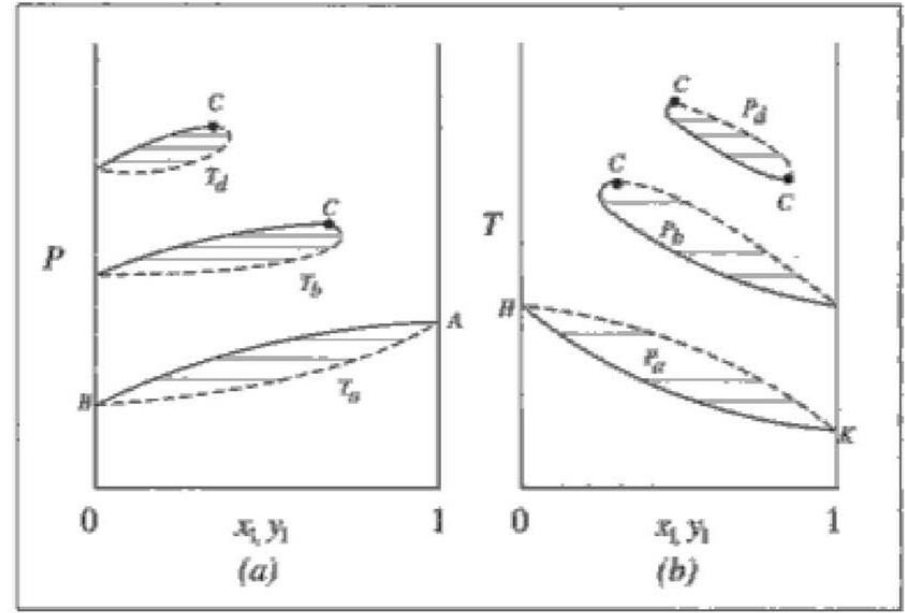
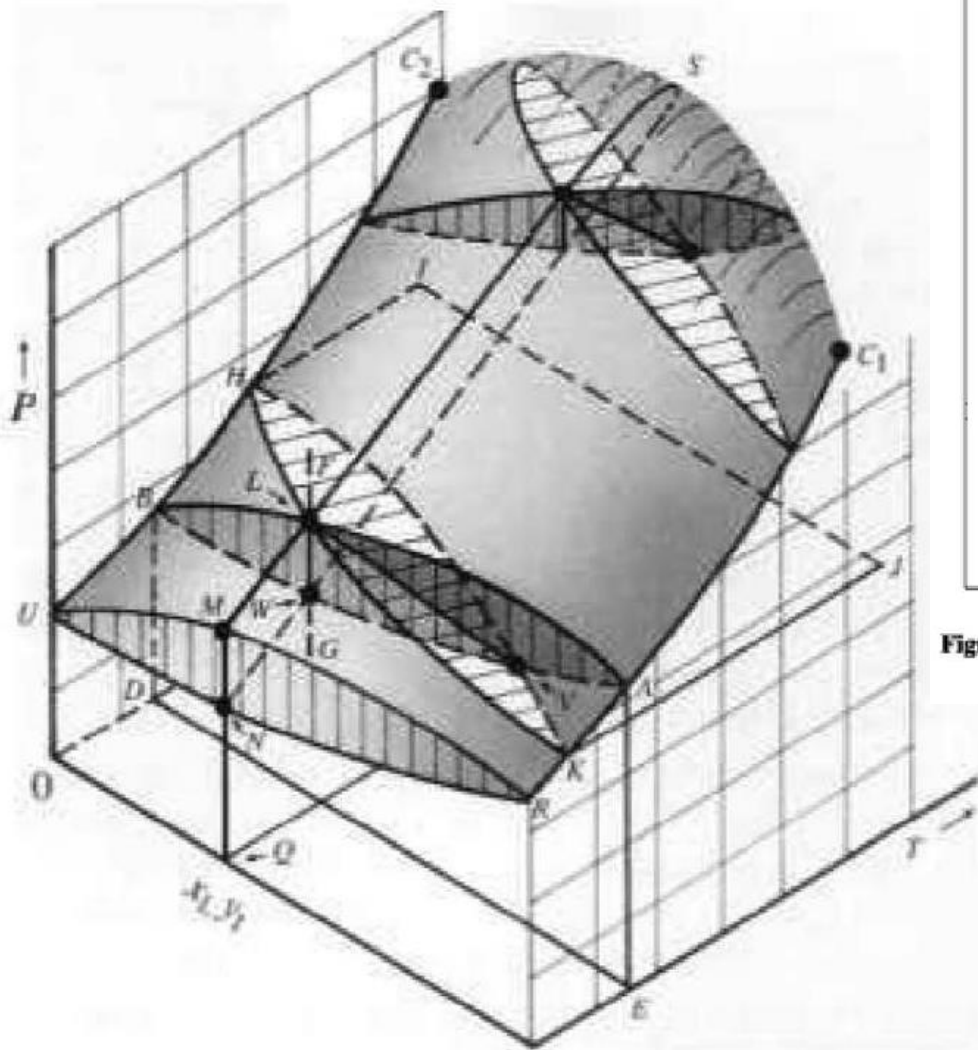
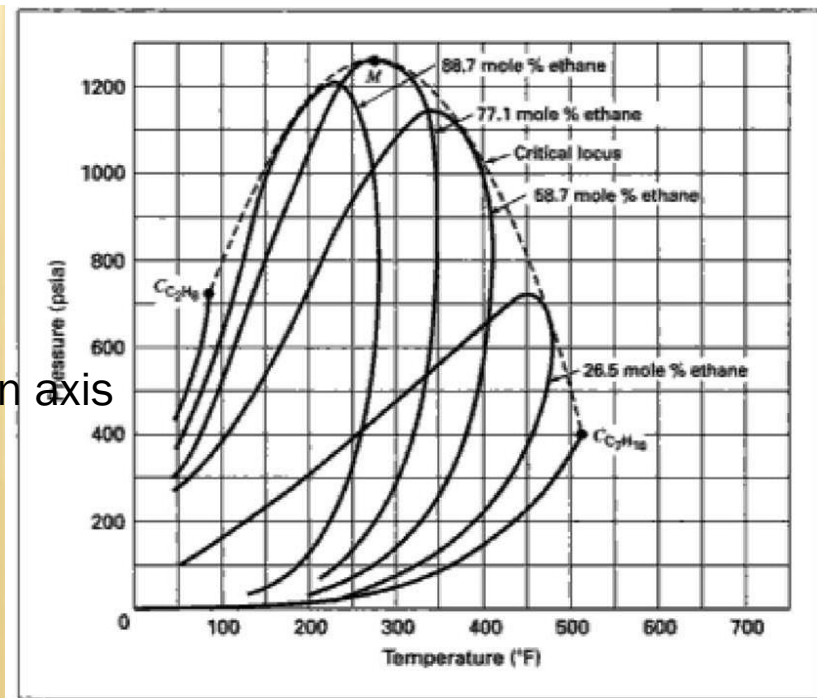


Figure 10.2: (a)  $Pxy$  diagram for three temperatures. (b)  $Txy$  diagram for three pressures.  
 — Saturated liquid (bubble line); - - - Saturated vapor (dew line)

When  $P$  is fixed, temperature varies along composition axis as an indirect function of vapor pressures

Temperature range is bounded by the saturation temperatures  $T_a^{sat}$ ,  $T_n^{sat}$  the temperatures at which pure species exert vapor pressures equal to  $P$   
 $T$ - $y$  variation can be plotted



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

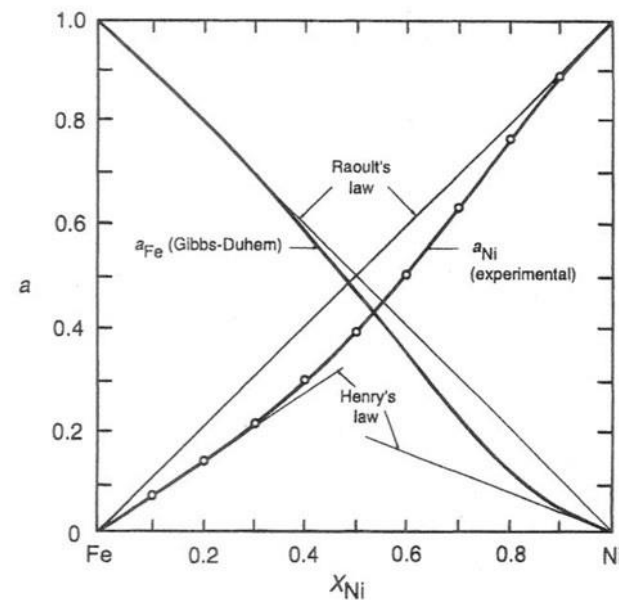
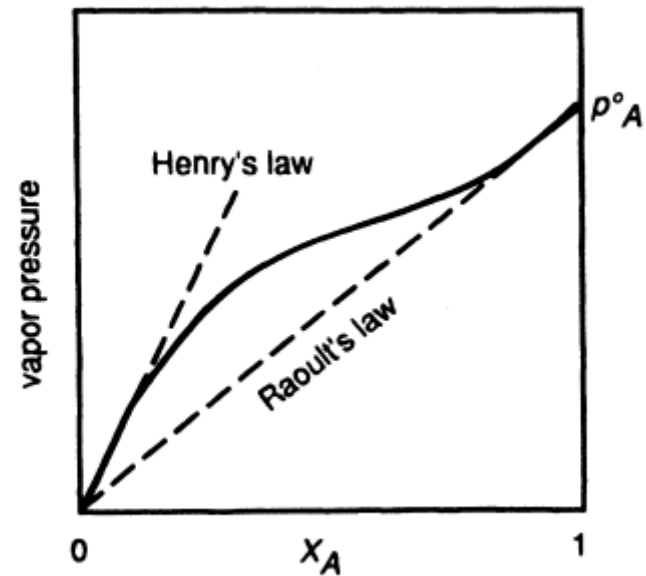


Figure 9.8 Activities in the system iron-nickel at 1600°C. (From G. R. Zellars, S. L. Payne, J. P. Morris, and R. L. Kipp, "The Activities of Iron and Nickel in Liquid Fe-Ni Alloys," *Trans. AIME* (1959), vol. 215, p. 181.)



Example – Carbonated water contains  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Determine the composition of the vapor phase in a sealed bottle of soda and the pressure exerted on the bottle at  $10^\circ\text{C}$  if the liquid phase mole fraction of  $\text{CO}_2$  is 0.01. Henry's constant for  $\text{CO}_2$  in water is about 990 bar.

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

Saturated water—Temperature table

Temp., $T$ °C	Sat. press., $P_{sat}$ kPa	Specific volume, $\text{m}^3/\text{kg}$		Internal energy, kJ/kg			Enthalpy, kJ/kg	
		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

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

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

Activity of ideal solutions equal the concentration of species so that

$$\gamma = \frac{P_i^{sat}}{P_i^o} = 1$$

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

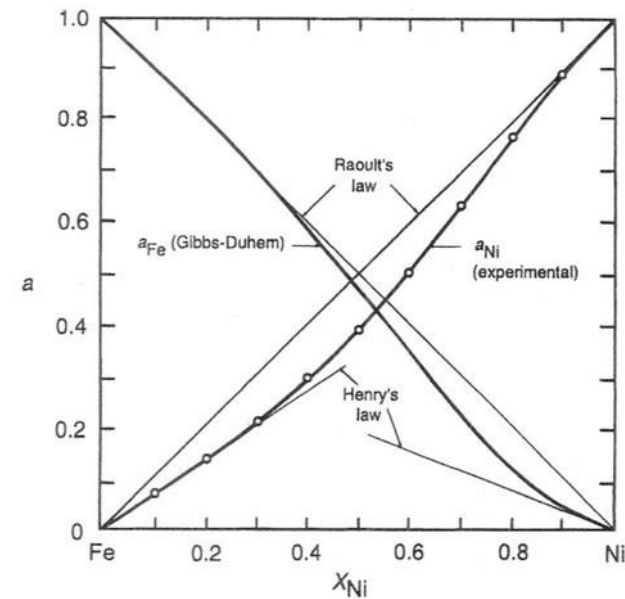


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## Relation between Raoult's and Henry's law

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

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

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

Derivation follows from partial Gibbs free energy equation:

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

$$\text{since } dG_A^P = RT d \ln a$$

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

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

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

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

$$a_A = \gamma_B x_A$$