

Property estimation from Pv-T behaviour

Real gas $\xrightarrow{I} \text{Ideal gas} \xrightarrow{II} \text{Ideal gas}$

T_1, P_1

T_1, P_1

T_1, P_2

$$\Delta h_1 = h(T_1, P_1) - h^\circ(T_1, P_1) = [\Delta h^\circ]_{T, P}$$

$$\Delta h_2 = 0$$



Real gas $\xleftarrow[IV]{T_2, P_2} \text{Ideal gas}$

IV

T_2, P_2

$$\Delta h_3 = \int_{T_1}^{T_2} c_p^\circ dT$$

$$\begin{aligned} \Delta h_4 &= h^\circ(T_2, P_2) - h(T_2, P_2) \\ &= -[\Delta h^\circ]_{T_2, P_2} \end{aligned}$$

M is an extensive property

ΔM^\ddagger

↳ Deviation from ideal gas

$$\Delta M^\ddagger|_{T, P} = M|_{T, P} - M^\ddagger|_{T, P}$$

This difference occurs because ; ideal gas properties are generally independent of pressure, while real gases depend on pressure.

$$(h - h^\circ)_{T, P} = \int_{P=0}^P \left(\frac{\partial h}{\partial P} \right)_T dP = \int_{P=0}^P \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP$$

$$(s - s^\circ)_{T, P} = \int_{P=0}^P \left[\left(\frac{\partial s}{\partial P} \right)_T + \frac{R}{P} \right] dP$$

$$= - \int_{P=0}^P \left[\left(\frac{\partial v}{\partial T} \right)_P - \frac{R}{P} \right] dP$$

$$(U - U_0) = (h - h_0) - P(V - V_0)$$

$$(A - A_0) = (U - U_0) - T(S - S_0)$$

$$(G - G_0) = (h - h^0) - T(S - S_0)$$

$$\Delta h^* = \int_{P=0}^P V dP - T \int_{P=0}^P \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$\Delta S^* = - \int_{P=0}^P \left(\frac{\partial V}{\partial T}\right)_P dP - \int_{P=0}^P R \frac{dP}{P}$$

w.k.t., $P = \frac{RT}{V-b} - \frac{a}{V^2}$

$$d(PV) = PdV + VdP$$

$$\Rightarrow VdP = d(PV) - PdV$$

$$\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1$$

$$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_P dP = - \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\begin{aligned} \Delta h^* &= \int_{RT}^{PV} d(PV) - \int_{V=V_0}^V P dV + T \int_{V_0}^V \left(\frac{\partial P}{\partial T}\right)_V dV \\ &= (PV - RT) + \int_{V_0}^V \cancel{T \left(\frac{\partial P}{\partial T}\right)_V} - \left(T \left(\frac{\partial P}{\partial T}\right)_V - P\right) dV \\ &\quad \downarrow \\ &= RT(z-1) \end{aligned}$$

$$\therefore \Delta h^{\ddagger} = (PV - RT) + \int_{V_0}^V \left(T \left(\frac{\partial P}{\partial T} \right)_V - P \right) dV$$

Similarly we get,

$$\Delta S^{\ddagger} = R \ln \frac{PV}{RT} + \int_{V_0}^V \left[\left(\frac{\partial P}{\partial T} \right)_V - \frac{R}{V} \right] dV$$

$$\begin{aligned} \Delta S^{\ddagger} &= R \ln \frac{P(V-b)}{RT} \\ \Delta h^{\ddagger} &= PV - RT - \frac{a}{V} \end{aligned} \quad \left. \begin{array}{l} \text{vander waals} \\ \text{Eqn. of state} \end{array} \right\}$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

Peng Robinson Eqn. of state

$$\frac{\Delta S^{\ddagger}}{R} = \ln \frac{V-b}{RT} - \frac{0.5a}{bRT^{1.5}} \ln \frac{V+b}{V}$$

$$\frac{\Delta h^{\ddagger}}{R} = -\frac{8}{2} \frac{A^2}{B} \ln \left(1 + \frac{b}{V} \right) + z - 1$$

We can define the above in the terms of compressibility factor,

$$\left[\frac{d(\Delta h^{\ddagger})}{dP} \right]_T = -RT^2 \int_b^P \left(\frac{\partial Z}{\partial T} \right)_P \frac{dP}{P}$$

$$= RT_r^2 T_C \int_0^P \left(\frac{\partial Z}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}$$

Similarly,

$$\Delta S^\circ = R \int_0^{P_r} \left[(z-1) + T_r \left(\frac{\partial z}{\partial T_r} \right)_{P_r} \right] \frac{dP_r}{P_r}$$

$$\frac{\Delta S^\circ}{R} = \int_0^{P_r} \left[(z-1) + T_r \left(\frac{\partial z}{\partial T_r} \right)_{P_r} \right] \frac{dP_r}{P_r}$$

$$\frac{\Delta h^\circ}{RT_c} = T_r^2 \int_0^{P_r} \left(\frac{\partial P}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}$$

Obey law of corresponding states

$$z = z^0 + w z' \xrightarrow{\text{correction}} \text{for complex}$$

↳ simple molecules

$$\Delta h^\circ |_{T_r, P} = - \frac{RT^2}{T_c} \int_0^{P_r} \left(\frac{\partial z^0}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}$$

$$- \frac{wRT^2}{T_c} \int_0^{P_r} \left(\frac{\partial z'}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}$$

$$\therefore \frac{\Delta h^\circ}{RT_c} = T_r^2 \int_0^{P_r} \left(\frac{\partial z^0}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}$$

$$\left(\frac{\Delta h^\circ}{RT_c} \right)' = T_r^2 \int_0^{P_r} \left(\frac{\partial z'}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}$$

$$\left(\frac{\Delta S^+}{R}\right)^0 = \int_0^{P_r} \left(z_0 - 1 + T_r \left(\frac{\partial z^0}{\partial T_r}\right)_{P_r}\right) \frac{dP_r}{P_r}$$

$$\left(\frac{\Delta S^+}{R}\right)^1 = w \int_0^{P_r} \left(z^1 + T_r \left(\frac{\partial z^1}{\partial T_r}\right)_{P_r}\right) \frac{dP_r}{P_r}$$

Eg:- $\Delta h^+_{CH_4}$ at $84^\circ C$ & 9.28 bar

$\Delta S^+_{CH_4}$

$$T_c = 190.7 K$$

$$P_c = 46.41 \text{ bar}$$

$$w = 0.011$$

$$T_r = \frac{305.15}{190.7} = 1.6 \quad P_r = \frac{9.28}{46.41} = 0.2$$

$$\frac{\Delta h^+}{RT_c}^0 = 0.085$$

$$\frac{\Delta h^+}{RT_c}^1 = 0.01$$

$$\frac{\Delta S^+}{R}^0 = 0.032$$

$$\frac{\Delta S^+}{R}^1 = 0$$

$$\begin{aligned} \therefore \frac{\Delta h^+}{RT_c} &= \frac{\Delta h^+}{RT_c}^0 + w \frac{\Delta h^+}{RT_c}^1 \\ &= 0.085 + (0.01)(0.011) \end{aligned}$$

$$\therefore \Delta h^+ = -0.135 \text{ kJ/mol}$$

At a low \rightarrow moderate pressure

$$z = \frac{P_r}{RT} = 1 + \frac{BP}{RT} = 1 + \frac{BP_c}{RT_c} \left(\frac{P_r}{T_r}\right)$$

$$v = \frac{RT}{P} \left(1 + \frac{BP}{RT}\right) = \frac{RT + B}{P}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial B}{\partial T} + \frac{B}{P}$$

$$\Delta H^\circ = \left(B - T \frac{dB}{dT} \right) P$$

$$\Delta S^\circ = - P \frac{dB}{dT}$$

$$B = \frac{RT}{Pc} (B_0^\circ + \omega B')$$

Thermodynamic Potentials

$$dU = TdS - PdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$



For closed system (with PV-work)

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n} dV + \left(\frac{\partial U}{\partial n}\right)_{S,P} dn$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,n} dS + \left(\frac{\partial H}{\partial P}\right)_{S,n} dP + \left(\frac{\partial H}{\partial n}\right)_{S,P} dn$$

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V,n} dT + \left(\frac{\partial A}{\partial V}\right)_{T,n} dV + \left(\frac{\partial A}{\partial n}\right)_{T,P} dn$$

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

$$\left(\frac{\partial U}{\partial n}\right)_{S,V} = u + n \left(\frac{\partial u}{\partial n}\right)_{S,V}$$

$$\left(\frac{\partial U}{\partial n}\right)_{S,V} \neq \left(\frac{\partial U}{\partial n}\right)_{S,V}$$

\downarrow
 $n \neq n'$

$$\left(\frac{\partial G}{\partial n}\right)_{T,P} = g + n \left(\frac{\partial g}{\partial n}\right)_{T,P} \quad G = ng$$

$$\left(\frac{\partial G}{\partial n}\right)_{T,P} = g$$

$$U = nU$$

$$dU = n du + u dn$$

$$= n (TdS - PdV) + Vdn$$

$$= n T ds - n P dV + u dn$$

$$= T d(nu) - S dn - P [d(nu) - Vdn] + u dn$$

$$dU = dn (u - Ts + Pv) - \underset{S}{Td} \underset{V}{(g/s)} - P d(nu)$$

$$dU = gdn - Tds - pdv$$

For single component open system

$$du = Tds - pdv + \gamma dn$$

$$dh = Tds + Vdp + \gamma dn$$

$$dA = -SdT - pdV + \gamma dn$$

$$dg = -SdT + Vdp + \gamma dn$$

Chemical Potential of a substance is its
molar/mass specific isobaric isothermal potential
where

$$\mu = \left(\frac{\partial U}{\partial n}\right)_{S,V} = \left(\frac{\partial H}{\partial n}\right)_{S,P} = \left(\frac{\partial A}{\partial n}\right)_{V,T} = \left(\frac{\partial g}{\partial n}\right)_{P,T}$$

Gibbs-Duhem Equation

$$s dT - v dp + n dy = 0$$

Multi comp. systems:

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial S}\right)_{V, n_j \neq i} dS + \left(\frac{\partial U}{\partial V}\right)_{S, n_j \neq i} dV + \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_1, \dots, n_{i-1}} dn_i \\ &\quad + \left(\frac{\partial U}{\partial n_j}\right)_{S, V, n_1, \dots, n_{i-1}} dn_j \\ &= \left(\frac{\partial U}{\partial S}\right)_{V, n} dS + \left(\frac{\partial U}{\partial V}\right)_{S, n} dV + \sum_{i=1}^n \mu_i dn_i \end{aligned}$$

$$s dT - v dp + \sum n_i dy_i = 0$$

$$\text{At const. } T \& P \quad \sum n_i dy_i = 0$$

$$\sum x_i dy_i = 0$$

$$x_1 dy_1 + x_2 dy_2 = 0 \quad (\text{Const. } T, P)$$

$$\mu_i = \left(\frac{\partial G_i}{\partial n_i}\right)_{T, P, n_j \neq i}$$

$$\sum x_i n_i = 0$$

$$dy \neq 0$$

$$\left(\frac{\partial \mu}{\partial n}\right)_{U,V} = -\frac{u}{T}$$

$$\left(\frac{\partial u}{\partial n}\right)_{U,V} = -\frac{u}{n^2} \quad \left(\frac{\partial u}{\partial n}\right)_{V,U} = -\frac{v}{n}$$

For only PV work from combined 1st and 2nd law, simple comp. system

$$TdS = du + PdV - \mu dn$$

Homogeneous Open Systems

$$dG_1 = \left(\frac{\partial G_1}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G_1}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G_1}{\partial n_1}\right)_{T,P} dn_1$$

Considering
Two phases

$n_1 \rightarrow$ no. of moles in P1

$n_2 \rightarrow$ no. of moles in P2

$$\text{At const. } P, T \quad \left(\frac{\partial G_1}{\partial n_1}\right) dn_1 + \left(\frac{\partial G_1}{\partial n_2}\right) dn_2 = 0$$

$$dn_1 + dn_2 = dn = 0 \Rightarrow dn_1 = -dn_2$$

$$\left(\left(\frac{\partial G_1}{\partial n_1}\right)_{T,P,n_2} - \left(\frac{\partial G_1}{\partial n_2}\right)_{T,P,n_1} \right) dn_1 = 0$$

$$dn_1 \neq 0 \quad \left(\frac{\partial G_1}{\partial n_1}\right)_{T,P,n_2} = \left(\frac{\partial G_1}{\partial n_2}\right)_{T,P,n_2}$$

$$\Rightarrow u_1 = u_2$$

If $\mu_1 > \mu_2$ $d\mu_1$ -ve \Rightarrow mass transfer occurs
from 1 \rightarrow 2

if $d\mu_2$ +ve mass transfer occurs
from 2 \rightarrow 1

$$d\mu_1 = dg = -S_1 dT + V_1 dP$$

$$d\mu_2 = dg = -S_2 dT + V_2 dP$$

Clapeyron Eqn:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \quad 0$$

S-L boundary $\Delta S = \Delta S_{\text{fusion}} = \frac{\Delta h_{\text{fusion}}}{T_{\text{fusion}}}$

$$\frac{dP}{dT} = \frac{\Delta h_f}{T \Delta V_{\text{fus}}}$$

$$P_2 = P_1 + \frac{\Delta h_f}{\Delta V_f} \ln \frac{T_2}{T_1}$$

L-V boundary

$$\frac{dP}{dT} = \frac{\Delta h_v}{T(V_v - V_l)} \quad V_v \gg V_l = \frac{RT}{P}$$

$$\frac{d(\ln P)}{dT} = \frac{\Delta h_{\text{vap}}}{RT^2} \Rightarrow \text{Clausius Clapeyron Eqn}$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta h_v}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

S-V boundary

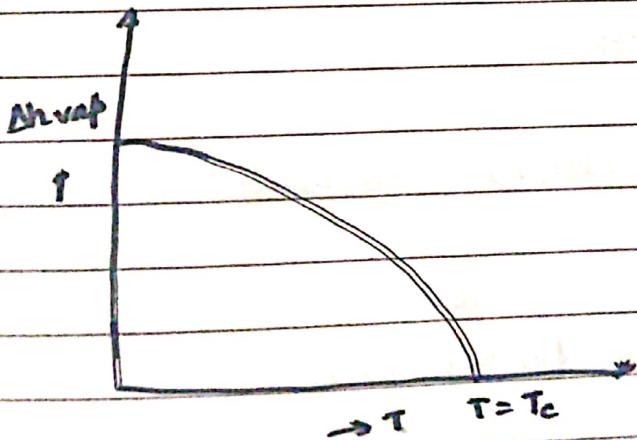
$$\frac{dP}{dT} = \frac{\Delta h_{sub}}{RT^2/P} = \Delta h_v + \Delta h_p$$

$$\log_{10} P = A - \frac{B}{T}$$

$$\Delta h_{vap} = \frac{RT^2}{P} \frac{dP}{dT}$$

$$\Delta h_{sub} = -2.303 R \frac{d \log P}{d(1/T)}$$

→ $\log_{10} P = A - \frac{B}{T+c} \Rightarrow \text{Antoine Eqn.}$



$$\frac{d(\Delta h_v)}{dT} = (c_{p,v} - c_{p,t}) + \frac{\Delta h_v - V_r B_r - V_L \beta_L}{V_r - V_L} \frac{\Delta h_v}{T}$$

↳ Kirchoff's eqn:

For ideal gas,

$$\frac{d(\Delta h_v)}{dT} = (c_{p,v} - c_{p,t})$$

S-L

$$\frac{d}{dT} \left(\frac{\Delta h_v}{T} \right) = C_{P,L} - C_{P,S}$$

→ Predict : Δh_v at temp. other than n.b.p
using Kirchoff's eqn:

Watson corr $\Delta h_{v_2} = \Delta h_{v_1} \left(\frac{1 - T_{r_2}}{1 - T_{r_1}} \right)^{0.38}$

Riedel corr. $\Delta h_{v,n} = 1.093 R T_c \left[T_{br} \frac{\ln P_c - 1.013}{0.93 - T_{br}} \right]$

↓
 T_b/T_c
B.P

Enthalpy of
vapourisation

Heterogeneous Closed Systems

π - phases ($1, \dots, \pi$)

c - component ($n = 1, \dots, c$)

For closed systems,

$$(dU)_{S,V} = 0 \quad (dA)_{V,T} = 0$$

$$(dH)_{S,P} = 0 \quad (dG)_{P,T} = 0$$

$$dU = \sum_{\alpha=1}^{\pi} T_{\alpha} dS^{\alpha} - \sum_{\alpha=1}^{\pi} \rho_{\alpha} dV^{\alpha} + \sum_{\alpha=1}^{\pi} \sum_{i=1}^c \mu_i^{\alpha} dm_i^{\alpha}$$

After solving we get,

$$T^1 = T^2 = \dots = T^{\pi}$$

$$\rho^1 = \rho^2 = \dots = \rho^{\pi}$$

$$\mu_1^1 = \mu_1^2 = \dots = \mu_1^{\pi}$$

$$\vdots$$

$$\mu_n^1 = \mu_n^2 = \dots = \mu_n^{\pi}$$

$$F = C - \pi + 2 \leftarrow \text{Gibbs Phase Rule}$$

Fugacity

$$S = -\left(\frac{\partial G}{\partial T}\right)_P, \quad V = \left(\frac{\partial G}{\partial P}\right)_T \Rightarrow 1^{\text{st}} \text{ order transition}$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = \left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial T}\right)_P\right]_P = \left(\frac{\partial S}{\partial T}\right)_P = \frac{c_p}{T}$$

$$\frac{\partial^2 G}{\partial T \partial P} = \beta V \Rightarrow 2^{\text{nd}} \text{ order transition}$$

For ideal gas,

$$dY = \frac{RT}{P} dP = RT d(\ln P) \rightarrow \text{pure comp.}$$

For real gas

$$dY = RT d(\ln f) \xrightarrow{\text{fugacity}}$$

$$\mu = RT \ln \frac{f_i}{f_i^0}$$

$$d(\ln f) = d(\ln P) + B_{sp}(T) dP +$$

Fugacity

Fugacity for a isothermal change for any component in any system, whether solid, liquid or gas

$$dY = RT d(\ln f) \text{ (const. temp.)}$$

$$\lim_{P \rightarrow 0} \frac{f_i}{P} = 1, \quad \lim_{P \rightarrow 0} \frac{f}{y_i P} = 1$$

The ratio $\alpha = f/f^{\circ}$ is called activity a

Gives the indication of how active a substance is relative to its std. state since it provides a measure of diff. between substance's chemical potential at the state of interest and that of standard state.

Concept of fugacity - the corrected pressure which for a comp. in a mix of ideal gases is equal to partial pressure of that comp.

- Fugacity is a measure of non-ideality of a gas
- Relation b/w fugacity and chemical potential is of conceptual aid in translating from thermodynamics to physical variables

2 phases α, β

$$\begin{aligned}\mu^\alpha &= \mu^{0\alpha} + RT \ln \frac{f^\alpha}{f^{0\alpha}} \\ \mu^\beta &= \mu^{0\beta} + RT \ln \frac{f^\beta}{f^{0\beta}}\end{aligned}\Rightarrow f^\alpha = f^\beta$$

Then

$$\mu^{0\alpha} - \mu^{0\beta} = RT \ln \frac{f^{0\alpha}}{f^{0\beta}}$$

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while equality of fugacity in all phases signifies chemical eq., the cond. that activities must be equal holds only for special cases where std. state in all phases are same.

$$\alpha_i = \frac{f_i}{f_i^0} \quad \phi = \frac{f_i}{P}$$

↑
fugacity
co-eff

$$\left[\frac{\partial \ln F}{\partial P} \right]_{T,n} = \frac{V}{RT}$$

$$\left[\frac{\partial \ln f}{\partial T} \right]_{P,n} = \frac{T(h^\circ - h)}{RT^2}$$

At low P

Molar enthalpy at given P

Increase in enthalpy due to expansion from pressure P to P_0 at const. tem.

$$\cdot h^\circ = \int C_p^\circ dT$$

For real gas, $d\gamma = RT \ln f = vdp$

For ideal gas, $d\mu^\circ = RT \ln P = \frac{RT}{P} dp$

Subtracting ① and ②

$$\gamma - \gamma^\circ = RT \ln \left(\frac{f}{P} \right) = \int_0^P \left(v - \frac{RT}{P} \right) dp$$

$$(OR) \ln \phi = \frac{1}{RT} \int_0^P \left(v - \frac{RT}{P} \right) dp$$

$$= (z-1) - \frac{1}{RT} \int_{v_0}^P P dv$$

Also $\frac{f}{P} \rightarrow 1$, as $P \rightarrow 0$

Fugacity co-efficient from PVT behaviour
of gases

Using van der Waals eqn: $\xrightarrow{\text{Using Z}}$

$$\ln \phi = \ln \left(\frac{f}{P} \right) = z - 1 - \frac{1}{RT} \int P dV$$

$$= z - 1 - \ln \frac{P(v-b)}{RT} - \frac{a}{RTv}$$

Using Redlich Kwong eqn:

$$\ln \phi = z - 1 - \ln(z-B) - \frac{a}{bRT} \ln \left(\frac{z+B}{z} \right)$$

Using Soave Redlich Kwong eqn:

$$\ln \phi = z - 1 - \ln(z-B) - \frac{a}{bRT} \ln \left(\frac{z+B}{z} \right)$$

Using Peng - Robinson eqn:

$$\ln \phi = z - 1 - \ln(z-B) - \frac{a}{2\sqrt{2} R b T} \ln \left(\frac{z+B(1+\sqrt{2})}{z+B(1-\sqrt{2})} \right)$$

HP

$$\int d \ln \left(\frac{f}{P} \right) = \int \frac{z-1}{P} dP$$

$$f/P = 1$$

$$\ln \left(\frac{f}{P} \right) = \int_0^P \frac{z-1}{P_r} dP_r$$

$\phi \rightarrow$ also agree with two par
law of corresponding states

$$\ln \phi = \ln \phi^0 + w \rightarrow \ln \phi' \\ \uparrow \text{charts}$$

Using Residual volume

$$\frac{\ln f}{P} = \frac{1}{RT} \int_0^P \frac{\Delta V^\circ}{RT} dP$$

$$RT \int_0^P d(\ln f) = \int_0^P dh - T \int_0^P ds$$

\downarrow

$C_P dT$

starting from zero
(so difficult to find at particular P)

$$RT \ln \frac{f}{f^0} = \Delta h^\circ - T \Delta S^\circ$$

Commonly used

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2} v(v+b)}$$

Redlich-Kwong

$$a = \frac{0.0427480 R^2 T_c^{2.5}}{P_c}$$

$$b = \frac{0.086640 R T_c}{P_c}$$

Fugacity of pure liquids

$$RT \ln \left(\frac{f}{P} \right) = \int_{P_{\text{sat}}}^P \left(v - \frac{RT}{P} \right) dP$$

liquid in eq. with vapour phase

since $f_{\text{vap}} = f_{\text{eq. sat}}$

condensed phase

$$= \int_0^P \left(v - \frac{RT}{P} \right) dP + \int_{P_{\text{sat}}}^P \left(v_c - \frac{RT}{P} \right) dP$$

$$RT \ln \frac{f^c}{P} = RT \ln \frac{f^{sat}}{P^{sat}} + \int_{P^{sat}}^P \frac{v^c dp}{RT} - RT \ln \frac{P}{P^{sat}}$$

$$f^c = P^{sat} \phi_v^{sat} \exp \left(\int_{P^{sat}}^P \frac{v^c dp}{RT} \right)$$

$$\Rightarrow \phi_v^{sat} = \frac{f^{sat}}{P^{sat}}$$

when f^c is very ^{low} _{high}, $f^{sat} = P^{sat} \Rightarrow \phi^{sat} = 1$,
 $v^c \neq f(P)$, in such cases

If P^{sat} is low $\phi_v^{sat} = 1$

$$f^c = P^{sat} \exp \left(\frac{v^c (P - P^{sat})}{RT} \right)$$

↓
Poynting correction factor
 ≈ 1

$\phi_v^{sat} < 1$ (In all other cases)

$$f^c = P^{sat} \quad (\text{P}^{sat} \text{ is low})$$

$$\ln \frac{f}{P} = z - 1 - \ln(z - BP) - \frac{A^2}{B} \ln \left(1 + \frac{BP}{z} \right) - ①$$

$$\text{where } \frac{PB}{RT} = BP, \frac{a}{bRT^{1.5}} = \frac{A^2}{B}$$

Cubic form,

$$\int z^3 - z^2 + BP \left(\frac{A^2}{B} - BP - 1 \right) z - \frac{A^2}{B} (BP)^2 = 0$$

On solving

largest z - saturated vap.

smallest z - saturated liq.

To find BP, we use the fact that liq and vapour are in eq.

We use ①

and we find the pressure at which liq and vap are in eq.

Mixtures

$$V_m \neq \sum n_i V_i$$

$$\hookrightarrow f(P, T, n_i, V_i)$$

Thermodynamic Properties of Real gas Mixtures

Mixing Rules

$$\left(P + \frac{a_m}{V_m^2} \right) (V_m - b_m) = RT$$

$$b_m^{1/3} = \sum_i y_i (b_i)^{1/3}$$

\hookrightarrow Binary mixture

$$a_m = \sum_{i,j} y_i y_j a_{ij} = f_n (a_{ii}, a_{ij}, a_{jj})$$

\downarrow
Interactions
btw molecules

a_{ij}

\hookrightarrow most cases $k_{ij} = 0$

$$a_m = \sum_{ij} y_i y_j \sqrt{a_{ii} a_{jj}} (1 - k_{ij})$$

\hookrightarrow binary interaction
btw comp.

Amagat's law of additive volume

$$N_m = \sum N_i V_i \text{ at same } T \text{ and } P$$

$$Z_m = \sum N_i Z_i$$

Dalton's law of additive pressure

$P = \sum P_i^o \rightarrow$ Pressure exerted by N_i moles
 of pure comp. gas i if
 it occupies the entire
 problem

Real gas $P_i^o \neq P_j$

Ideal gas $P_i^o = P_j$

$$Z_M' = \frac{PV}{NRT} = \frac{V}{NRT} \sum P_i^o = \sum \frac{N_i}{N} \left(\frac{P_i V}{N_i RT} \right)$$

\uparrow Defn
from Amagat's law

$$= \sum y_i z_i'$$

$$Z_M = \sum y_i z_i \quad \text{at system temp & pressure}$$

$$RT \ln \hat{\phi}_m = RT \ln \frac{f_m}{P} = \int_0^P \left(v_m - \frac{RT}{P} \right) dP$$

Fugacity for comp i in a mixture

$$RT \ln \hat{\phi}_i = RT \ln \frac{f_i}{P} = \int_0^P \left(\left(\frac{\partial v_i}{\partial n_i} \right)_{T, P, n_j \neq i} - \frac{RT}{P} \right) dP$$

$$\text{For pure comp. } \rightarrow \left(\frac{\partial v}{\partial n} \right)_{T, P} = v$$

Partial Molar properties

Partial Molar quantity (\bar{y}_i) is a measure of how much the total property (y) changes when n_i is changed, keeping T, P and other mole numbers fixed ($n_{j \neq i}$)

$$\bar{y}_i = \bar{y}_i(T, P, n_1, n_2) = \left(\frac{\partial y}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

characteristic

$$\bar{v}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

$$\bar{s}_i = \left(\frac{\partial S}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

$$\bar{h}_i = \left(\frac{\partial H}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

$$\bar{g}_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}} = \mu_i$$

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_{j \neq i}} = \left(\frac{\partial H}{\partial n_i} \right)_{S, P, n_{j \neq i}} = \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_{j \neq i}}$$

$$\sum n_i d\bar{v}_i = 0 \Rightarrow \text{Gibb's Duhem eqn. in}$$

$\bar{y}_i \leftarrow$ partial molar prop

$$\Rightarrow \sum \mu_i dy_i = 0$$

$$\sum n_i dy_i = 0$$

$$\alpha_1 d\bar{m}_1 + \alpha_2 d\bar{m}_2 = 0$$

$$d\bar{m}_1 = -\frac{\alpha_2}{\alpha_1} d\bar{m}_2$$

Consider $\bar{m}_1 \rightarrow \text{known}$

$$\bar{m}_2 = ?$$

$$\int_0^{\bar{m}_2} d\bar{m}_2 = - \int_0^{\bar{m}_1} \left(\frac{\alpha_2}{\alpha_1} \right) d\bar{m}_1$$

$$\therefore \bar{m}_2 = - \int_0^{\bar{m}_1} \left(\frac{\alpha_2}{\alpha_1} \right) d\bar{m}_1$$

$$\bar{m}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

Experimental determination of \bar{m}_i

→ Method of intercepts (Binary system)

$$V = \frac{V}{n_A + n_B}$$

$$V = \eta \theta (n_A + n_B)$$

$$\bar{v}_A = \left(\frac{\partial V}{\partial n_A} \right)_{T, P, n_B} = \frac{\partial}{\partial n_A} [\eta \theta (n_A + n_B)]_{T, P, n_B}$$

$$\bar{v}_A = \bar{v} + (n_A + n_B) \left(\frac{\partial v}{\partial n_A} \right)_{T, P, n_B}$$

$$\left(\frac{\partial v}{\partial n_A} \right)_{n_B} = \left(\frac{\partial v}{\partial n_B} \right)_{n_B} \left(\frac{\partial x_B}{\partial n_A} \right)_{n_B}$$

$$\therefore - \left(\frac{\partial \bar{v}}{\partial x_B} \right) \left(\frac{n_B}{(n_A + n_B)^2} \right)$$

$$\bar{v}_A = v + (n_A + n_B) \left(\frac{\partial v}{\partial n_A} \right)_{T, P, n_B}$$

$$\bar{v}_B = v - x_B \left(\frac{\partial v}{\partial x_B} \right)$$

$$v = \bar{v}_A - x_B \left(\frac{\partial v}{\partial x_B} \right)$$

$$w = \bar{v}_B - (1-x_B) \left(\frac{\partial v}{\partial x_B} \right)$$

$$v = \bar{v}_A, x_B = 0$$

$$v = \bar{v}_B, x_A = 0 (x_B = 1)$$

$$\bar{g}_i = \left(\frac{\partial G_i}{\partial n_i} \right)_{T, P, n_{i+j}} = u_i$$

$$dG = \sum \left(\frac{\partial G_i}{\partial n_i} \right) dn_i = \sum u_i dn_i$$

$$u_A dn_A + u_B dn_B = dw_{\text{non-}PV}$$

Total property = \bar{m}_i

Molar property = $\frac{\bar{m}_i}{n} = m_i$

Partial molar property = \bar{m}_i in α -phase

$$u = \sum n_i m_i \quad f_m = \sum x_i \bar{f}_i$$

$$m_i = \sum x_i \bar{m}_i$$

Partial molar fugacity

$$\left(\frac{f_m}{P} \right)_i = \prod_{i=1}^c \left(\frac{\hat{f}_i}{y_i P} \right)^{y_i}$$

Ideal Solutions

$$x_i p_i^{\text{sat}} = y_i p$$

- ① Ideal soln' are formed with no change in vol.
- ② Molar enthalpy of mixing is zero,

$$\Delta V_m = 0$$

$$\Delta h_m = 0$$

$$\Delta U_m = 0$$

$$\Delta g_m = RT \sum_{i=1}^C x_i \ln x_i \quad \left[\frac{\partial \text{int}}{\partial T} \right]_{P,n} = \frac{n^o - b}{RT^2}$$

$$\Delta S_m = - R \sum_{i=1}^C x_i \ln x_i$$

$$P_i^s = x_i P_i^s$$

Phase Eqn:

$$\hat{f}_i^L = x_i f_i^L$$

$$\hat{f}_i^V = y_i f_i^V$$

If $\sum_{i=1}^L$ phases are in eq.

$$x_i f_i^L = y_i f_i^V$$

At low to moderate pressure,

$$\hat{f}_i^V = y_i p, \quad \hat{f}_i^L = x_i p_i^{\text{sat}}$$

$$\sum x_i = 1, \quad \sum y_i = 1$$

$$y_1 = \frac{\alpha x_1}{1 + (\alpha - 1)x_1} \quad \alpha = \frac{P_2^{\text{sat}}}{P_1^{\text{sat}}}$$

$$\frac{P_2}{P_1} = \frac{\alpha x_2}{1 - x_2}$$

→ Calculate P_i^s at known T

$$K_i = \frac{y_i}{x_i} = \frac{P_i^s}{P} \quad F \rightarrow \boxed{\text{Partial}} \quad \begin{array}{l} \text{Vapour Stream} \\ V, y, P, T \end{array}$$

↓
Liquid stream
 $L \propto T_i P$

$$x_i = \frac{Z_{F,i}}{Z_F}$$

$$\left(\frac{L}{F} \right) + \left(1 - \frac{L}{F} \right) k_i$$

Non-ideal soln.

$$\begin{aligned} \Delta g_{M,\text{real}} &= g_{\text{after}} - g_{\text{before}} \\ &= \sum x_i \bar{g}_i - \sum x_i g_i \\ &= \sum x_i \underbrace{(\bar{g}_i - g_i)}_{\hookrightarrow \bar{g}_i^E} = \sum x_i RT \ln \frac{\bar{f}_i}{f_i} \end{aligned}$$

$$g_E^E = \sum x_i \bar{g}_i^E$$

$$\bar{g}_i^E = RT \cancel{x_i} \ln \bar{y}_i \quad \bar{g}_i^E = x_i \ln \bar{x}_i$$

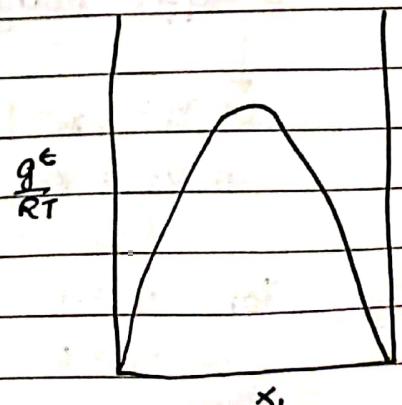
For binary mixture,

$$\frac{g^E}{RT} = x_1 \ln \bar{y}_1 + x_2 \ln \bar{y}_2$$

$$\frac{g^E}{RT} \text{ at } x_1 = 0 \text{ is } 0$$

$$\frac{g^E}{RT} \text{ at } x_2 = 0 \text{ is } 0$$

$$\begin{aligned} \frac{g^E}{RT} &= f(x_1, x_2) \\ &= A x_1 x_2 \end{aligned}$$



$$\ln \gamma_i = \frac{\bar{g}_i^E}{RT} \quad \bar{g}_i^E = \left(\frac{\partial G^E}{\partial n_i} \right)_{T, P, n_j \neq i}$$

$$\bar{g}_i^E = \left(\frac{\partial n g_i^E}{\partial n_i} \right)_{T, P, n_2} = \left(\frac{\partial (n_1 + n_2) g^E}{\partial n_i} \right)_{T, P, n_2}$$

$$\frac{\bar{g}_i^E}{RT} = A \left(\frac{\partial (n_1 + n_2)}{\partial n_i} \left(\frac{n_1}{n_1 + n_2} \right) \frac{n_2}{(n_1 + n_2)} \right)_{T, P, n_2}$$

$$= A \left(\frac{\partial}{\partial n_i} \left(\frac{n_1 n_2}{n_1 + n_2} \right) \right)_{T, P, n_2}$$

$$= A \left(\frac{n_2 (n_1 + n_2) - n_1 n_2}{(n_1 + n_2)^2} \right)$$

$$\frac{\bar{g}_i^E}{RT} = A \left(\frac{n_2}{(n_1 + n_2)} - \frac{n_1 n_2}{(n_1 + n_2)^2} \right)$$

$$= A x_2 - A x_1 x_2$$

$$= A x_2^2$$

$$\ln \gamma_1 = A x_2^2$$

$$\ln \gamma_2 = A x_1^2$$

→ Redlich-Kister Eqn:

$$\frac{g^E}{RT} = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \dots]$$

↳ Temp-dependent

3 Suffix Margules Eqn: $\frac{g^E}{RT} = x_1 x_2 [Bx_1 + Ax_2]$

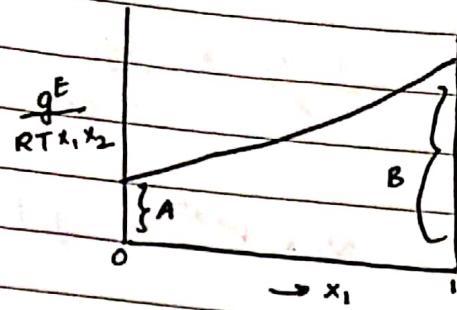
$$\ln \gamma_1 = x_2^2 [A + 2(B-A)x_1]$$

$$\ln \gamma_2 = x_1^2 [B + 2(A-B)x_2]$$

For $x_1 = 1 \quad \ln \gamma_1 = 0 \quad A = \ln \gamma_1 \quad x_2 = 1$

$x_1 = 0 \quad \ln \gamma_2 = 0 \quad B = \ln \gamma_2 \quad x_1 = 1$

$$\frac{g^E}{RTx_1x_2} = Bx_1 + Ax_2$$



van Laar Equation

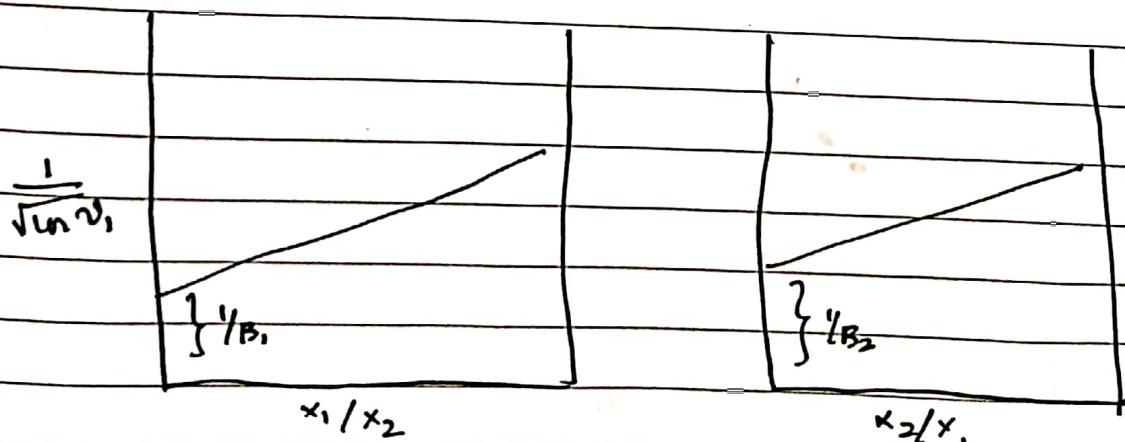
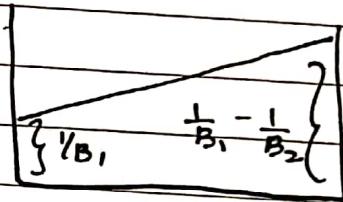
$$\frac{g^E}{RT} = \frac{Bx_1x_2}{x_1 \left(\frac{B_1}{B_2} \right) + x_2}$$

$$\ln \gamma_1 = \frac{-\bar{g}_1^E}{RT} = \frac{\partial}{\partial n_1} \left(\frac{n g_E}{RT} \right)$$

$$= \frac{B_1}{\left(1 + \frac{B_1}{B_2} \frac{x_1}{x_2} \right)^2}$$

$$\ln \gamma_2 = \frac{B_2}{\left(1 + \frac{B_2}{B_1} \frac{x_2}{x_1} \right)^2}$$

$$\frac{x_1x_2}{(g_E^E / RT)} = \frac{1}{B_1} + x_1 \left(\frac{1}{B_1} - \frac{1}{B_2} \right)$$



For low to moderate Pr (Raoult's law)

$$\text{At point of azeotropy, } \frac{dp_1}{dx_1} = \frac{dp_2}{dx_2} \Rightarrow \frac{x_2}{x_1} = \frac{P_2}{P_1}$$

$$\frac{1-x_1}{x_1} = \frac{y_1}{1-y_1} \Rightarrow x_1 = y_1$$

$$v_1, x_1, p_1^{\text{sat}} = y_1, P$$

$$v_1 = \frac{P}{p_1^{\text{sat}}}$$

$$v = \frac{P}{p_2^{\text{sat}}}$$

k-factor

$$k_i = \frac{y_i}{x_i}$$

$$\textcircled{1} \quad x_1 r_1 p_i^{\text{sat}} = y_1 p$$

a) Margules eqn:

$$\frac{g^E}{x_1 x_2 RT} = B x_1 + A x_2$$

$$B = \left(2 - \frac{1}{x_2} \right) \frac{\ln r_1}{x_2} + 2 \frac{\ln r_2}{x_1}$$

$$A = \left(2 - \frac{1}{x_1} \right) \frac{\ln r_2}{x_1} + 2 \frac{\ln r_1}{x_2}$$

$$(0.212) r_1 \times p_i^{\text{sat}} = (0.599) \times 518$$

$$r_1 p_i^{\text{sat}} = 1463.594 \text{ Torr}$$

$$\log_{10} p_i^{\text{sat}} = A + \frac{B}{T + C}$$

$$= 8.37895 - \frac{1788.02}{227.438 + 95}$$

$$= 2.83364$$

$$p_i^{\text{sat}} = 681.7668212 \text{ Torr}$$

$$r_1 = 2.14676$$

$$0.788 r_2 p_2^{\text{sat}} = 0.401 \times 518$$

$$p_2^{\text{sat}} = 10 (A - B/T + C)$$

$$= 10 (7.17294 - 1599.2/98 + 229.26)$$

$$= 10 (2.3953)$$

$$p_2^{\text{sat}} = 248.4806 \text{ Torr}$$

$$r_2 = \frac{0.401 \times 518}{248.4806 \times 0.188} = 1.0609$$

$$B = \left(2 - \frac{1}{0.788} \right) \frac{\ln(2.14676)}{0.788} + 2 \frac{\ln(1.0609)}{0.212}$$

$$= (0.73096)(0.969492) + 0.557713 \\ = 1.26637$$

$$A = \left(2 - \frac{1}{0.212} \right) \frac{\ln(1.0609)}{0.212} + 2 \times \frac{\ln(2.14676)}{0.788}$$

$$= (-2.71698)(0.27886) + 1.938984 \\ = 1.18132$$

$$\frac{g_E}{RT} = x_1 x_2 (1.26637 x_1 + 1.18132 x_2)$$

5) Van Laar Eqn:

$$\ln(\gamma_1) = \frac{B_1}{\left(1 + \frac{B_1 x_1}{B_2 x_2}\right)^2}$$

$$\ln(\gamma_2) = \frac{B_2}{1 + \left(\frac{B_2 x_2}{B_1 x_1}\right)^2}$$

$$\ln(2.14676) = \frac{B_1}{\left(1 + \frac{B_1 (0.2694)}{B_2}\right)^2}$$

$$\ln(1.0609) = \frac{B_2}{\left(1 + \frac{B_1 (3.71698)}{B_2}\right)^2}$$

$$+ SAT \bar{v} dp + \sum n_i d\hat{v}_i = 0$$

$$\mu = \frac{G}{n}$$

$$s^E dT - v^E dp + \sum x_i d\bar{q}_i^E = 0$$

$$d\bar{q}_i^E = RT \ln \varphi_i$$

$$\frac{h^E}{T} - g^E dT - v^E dp + \frac{g^E}{T} + \sum x_i d\ln \varphi_i = 0$$

$$\frac{h^E}{T} dT - v^E dp + \sum x_i d\ln \varphi_i = 0$$

At const. T, P

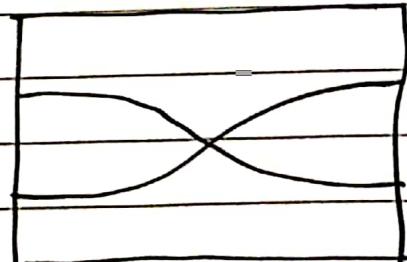
$$\sum x_i d\ln \varphi_i = 0$$

For binary mixture

$$\left(\frac{d \ln \varphi_1}{dx_1} \right)_{T, P} = - \frac{x_2}{x_1} \left(\frac{\partial \ln \varphi_2}{\partial x_1} \right)_{T, P}$$

$$x_1 = 1, x_2 = 0 \Rightarrow \frac{d \ln \varphi_1}{dx_1} = 0$$

$$\int_{x_2=0}^{x_2} d \ln \varphi_2 = - \int_{x_1=0}^{x_1} \frac{x_2}{x_1} d \ln \varphi_1$$



$$\ln \varphi_2|_{x_2} - \ln \varphi_2|_{x_2=0} = \int_{x_1=0}^{x_1} -\frac{x_1}{x_2} d \ln \varphi_1$$

$$\frac{g^E}{RT} = \alpha_1 \ln v_1 + \alpha_2 \ln v_2$$

$$d\left(\frac{g^E}{RT}\right) = \alpha_1 d(\ln v_1) + \ln v_1 dx_1 + \alpha_2 d(\ln v_2) + \ln v_2 dv_2$$

$$\sum \alpha_i d(\ln v_i) = -\frac{h^E}{RT^2} dT + \frac{v^E}{RT} dP$$

$$\alpha_1 d(\ln v_1) + \alpha_2 d(\ln v_2) = -\frac{h^E}{RT^2} dT + \frac{v^E}{RT} dP$$

$$d\left(\frac{g^E}{RT}\right) = \ln\left(\frac{v_1}{v_2}\right) dx_1 - \frac{h^E}{RT^2} dT + \frac{v^E}{RT} dP$$

$$x_1=1 \quad T(x_1=1) \quad P(x_1=1)$$

$$\int_{x_1=0}^{x_1=1} \ln\left(\frac{v_1}{v_2}\right) dx_1 = \int_{T(x_1=0)}^{T(x_1=1)} \frac{h^E}{RT^2} dT - \int_{P(x_1=0)}^{P(x_1=1)} \frac{v^E}{RT} dP$$

At constant T, P

$$x_1=1 \quad \int_{x_1=0}^{x_1=1} \ln\left(\frac{v_1}{v_2}\right) dx_1 = 0$$

