General
Info

EQUATIONS

$dU^t = dQ - dW$ $\quad t$ = total

$dQ_{REV} = T dS^t$, $dW_{REV} = -P dV^t$

$dU^t = T dS^t + -P dV^T$

$H = U + PV$, $A = U - TS$, $G = H - TS$

$$\left.\begin{aligned} dU &= T dS + P dV \\ dH &= T dS - V dP \\ dA &= -P dV - S dT \\ dG &= V dP - S dT \end{aligned}\right\} \text{1ST AND 2ND LAW}$$

$$\left.\begin{aligned} T &= \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P \\ -P &= \left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T \\ V &= \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T \\ -S &= \left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P \end{aligned}\right\} \text{MAXWELL'S RELATIONS}$$

$$\left.\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial V}\right)_V \\ \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P \\ \left(\frac{\partial P}{\partial T}\right)_V &= \left(\frac{\partial S}{\partial V}\right)_T \\ \left(\frac{\partial V}{\partial T}\right)_P &= -\left(\frac{\partial S}{\partial P}\right)_T \end{aligned}\right\} \text{MAXWELL EQUATIONS}$$

ASSUMPTIONS, RESTRICTIONS

- 1ST LAW, DIFFERENTIAL FORM, CLOSED (CONSTANT MASS SYSTEM)
- RESULT OF 2ND LAW, REVERSIBLE
- 1ST + 2ND LAW, CONSTANT MASS, CHANGE FROM ONE EQUIL STATE TO ANOTHER
- THERMODYNAMIC DEFINITIONS
- HOMOGENEOUS FLUID OF CONSTANT COMPOSITION (ONE PHASE)
- DERIVED BY COMPARING 1ST AND 2ND LAW TO TOTAL DIFFERENTIAL OF dU, dH, dA, dG
- DERIVED FROM CRITERION OF EXACTNESS $\left(\frac{\partial M}{\partial x \partial y}\right) = \left(\frac{\partial N}{\partial y \partial x}\right)$ APPLIED TO 1ST & 2ND LAW

$U = Q - W$ $\quad H = U + PV$

$dQ = TdS$ $\quad G = H - TS$

$dW = -PdV$

SMITH AND VAN NESS CHAP. 6

Equations

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

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

$$H = H_0' + \int_{T_0}^{T} C_p' \, dT - \Delta H'$$

$$\Delta H' = \int_0^P \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] dP \qquad \text{const } T$$

T_0, S_0, H_0 are arbitrary

$$S = S_0' + \int_{T_0}^{T} \frac{C_p'}{T} dT - R \ln \frac{P}{P_0} - \Delta S'$$

$$\Delta S' = \int_0^P \left[\left(\frac{\partial V}{\partial T}\right)_P - \frac{R}{P}\right] dP \qquad \text{const } T$$

$$\frac{dP^{SAT}}{dT} = \frac{\Delta H^{\alpha\beta}}{T \Delta V^{\alpha\beta}}$$

α, β are phases

$$\Delta H^{VAP} = \frac{-R \, d(\ln P^{SAT})}{d(1/T)}$$

$$M = (1-x) M_f + x M_g$$

Assumptions, Restrictions

Found from 1ST and 2ND laws

II

- gives actual enthalpy from ideal gas C_p data and PVT data of a fluid
- prime indicates ideal gas property
- gives actual entropy from ideal gas C_p data and PVT data of a fluid.

- Clapeyron equation, derived from $dG^\alpha = dG^\beta$ and 1ST, 2ND law in form of dG.
- Clausius-Clapeyron eqn
  - assumes ideal gas and $V_{liq} \ll V_{gas}$
- gives properties of a 2-phase mixture of a pure component.

EQUATIONS

ASSUMPTIONS, RESTRICTIONS

All the below is for the ideal solution Pg 213

$$d(nU) = T\,d(nS) + P\,d(nV) + \Sigma(\mu_i\,dn_i)$$

$$d(nH) = T\,d(nS) + nV(dP) + \Sigma(\mu_i\,dn_i)$$

$$d(nA) = -(nS)dT - P\,d(nV) + \Sigma(\mu_i\,dn_i)$$

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

$$\mu_i = \left[\frac{d(nU)}{dn_i}\right]_{nS,nV,n_j} = \left[\frac{\partial(nH)}{\partial n_i}\right]_{nS,P,n_j} = \left[\frac{\partial(nA)}{\partial n_i}\right]_{nV,T,n_j} = \left[\frac{\partial(nG)}{\partial n_i}\right]_{T,P,n_j}$$

- defn of chemical potential

$$* \quad \bar{M}_i = \left(\frac{\partial(nM)}{\partial n_i}\right)_{T,P,n_j} \qquad nM = \Sigma n_i \bar{M}_i \quad \& \quad M = \Sigma x_i \bar{M}_i$$

- defn of PARTIAL MOLAR PROPERTY

$$\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \left(\frac{\partial M}{\partial P}\right)_{T,x} dP - \Sigma(x_i\,d\bar{M}_i) = 0$$

- Gibbs-Duhem equation
- valid for any homogeneous phase

$$d(nM) = n\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + n\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \Sigma(\bar{M}_i\,dn_i)$$

$$\bar{M}_i = M - \sum_{k \neq i}\left[x_k\left(\frac{\partial M}{\partial x_k}\right)_{T,P,x_{l\neq i,k}}\right]$$

- Relates the PARTIAL MOLAR PROPERTY TO THE MOLAR PROPERTY OF THE SOLUTION AND TO MOLE FRACTIONS.

$$\bar{M}_i = M_i \quad \text{at } x_i \to 1$$
$$= \bar{M}_i^{\infty} \quad \text{as } x_i \to 0$$

$$M_i = \left[\frac{\partial(nM)}{\partial n_i}\right]_{T,P,n_j}; \quad nM = \Sigma(nM_i) \; ; \quad M = \Sigma(x_i M_i) \; *$$

- This is ONLY FOR ideal solutions

* $M \Rightarrow$ SOLUTION PROPERTIES
$\bar{M}_i \Rightarrow$ PARTIAL PROPERTIES
$M_i \Rightarrow$ PURE COMPONENT PROPERTIES

* Every equation relating molar thermodynamic properties for a CONSTANT COMPOSITION solution has as a counterpart an analogous equation relating the corresponding partial molar properties. For each component in the solution

CHAP. 1

EQUATIONS

$$d\bar{G}_i = RT\, d\ln f_i \quad \text{or} \quad d\bar{G}_i = RT\, d\ln \hat{f}_i$$

$$\lim_{P\to 0} \frac{f_i}{P} = 1 \quad \text{or} \quad \lim_{P\to 0} \frac{\hat{f}_i}{x_i P} = 1$$

$$\hat{f}_i = x_i P$$

$$\phi_i = \frac{f_i}{P} \qquad \hat{\phi}_i = \frac{\hat{f}_i}{x_i P}$$

$$\ln \phi_i = \int_0^P (Z_i - 1)\frac{dP}{P} \quad (\text{const } T)$$

$$\ln \phi_i = \frac{-1}{RT}\int_0^P \Delta V_i'\, dP \quad (\text{const } T)$$

} for gases generally

$$\ln \hat{\phi}_i = \frac{-1}{RT}\int_0^P \left(\frac{RT}{P} - \bar{V}_i\right) dP$$

$$\ln \frac{f_i}{f_i^*} = \frac{1}{RT}(G_i - G_i^*) = \frac{1}{R}\left[\frac{H_i - H_i^*}{T} - (S_i - S_i^*)\right]$$

$$\ln \phi = \frac{\Delta S'}{R} - \frac{\Delta H'}{RT} \qquad (A)$$

$$\ln \frac{f_i}{f_i^{SAT}} = \frac{1}{RT}\int_{P_i^{SAT}}^P V_i\, dP$$

$$\left(\frac{d\ln f_i}{dT}\right)_{P,x} = \frac{\Delta H_i'}{RT^2}$$

ASSUMPTIONS, RESTRICTIONS

- Derived from 1st, 2nd law in dG
- Defn of fugacity
- Ideal gas assumption
- Defns of fugacity coefficient
- ways of calculating ϕ_i
- $\hat{\phi}_i \leftrightarrow \phi_i$
  $\bar{z}_i \leftrightarrow z_i$
- derived from $dG_i = +V_i\, dP = RT\, d\ln f_i$
  and from $\phi_i = \frac{f_i}{P}$

- for a liquid!

- derived from (A)
- gives effect of temp on f_i

EQUATIONS

$$\bar{f}_i^{id} = x_i f_i^\circ$$

$$\neq \lim_{x_i \to 1} \frac{\bar{f}_i}{x_i} = f_i \qquad \text{Lewis-Randall rule}$$

$$\neq \lim_{x_i \to 0} \frac{\hat{f}_i}{x_i} = k_i \qquad \text{Henry's law}$$

7-5 Mixing Property Changes

$$\Delta M = M - \sum x_i M_i^\circ$$

$$\Delta \bar{M}_i = \bar{M}_i - M_i^\circ$$

$$\Delta M = \sum x_i \Delta \bar{M}_i$$

eg.

$$\frac{\Delta G}{RT} = \frac{1}{RT} \sum [\bar{G}_i - G_i^\circ] x_i = \text{same}$$

$$\frac{P\Delta V}{RT} = \frac{P}{RT} \sum [x_i (\bar{V}_i - V_i^\circ)] = \frac{1}{RT} \sum \left\{ x_i \left[\frac{\partial (\bar{G}_i - G_i^\circ)}{\partial \ln P} \right]_{T,x} \right\}$$

$$\frac{\Delta H}{RT} = \frac{1}{RT} \sum [x_i (\bar{H}_i - H_i^\circ)] = \frac{1}{RT} \sum \left\{ x_i \left[\frac{\partial (\bar{G}_i - G_i^\circ / RT)}{\partial \ln T} \right]_{P,x} \right\}$$

$$\frac{\Delta S}{R} = \frac{1}{R} \sum [x_i (\bar{S}_i - S_i^\circ)] = -\frac{1}{RT} \sum \left\{ x_i \left[\frac{\partial (\bar{G}_i - G_i^\circ)}{\partial \ln T} \right]_{P,x} \right\}$$

$$\bar{G}_i - G_i^\circ = RT \ln \frac{\hat{f}_i}{f_i^\circ}$$

$$\hat{a}_i = \frac{\hat{f}_i}{f_i^\circ}$$

substitute

ASSUMPTIONS, RESTRICTIONS

- fugacity of component i in an IDEAL solution
- f_i° is the fugacity of component i IN A STANDARD STATE.

M_i° = molar property of i in a specified standard state.

M = property of a solution

$\Delta \bar{M}_i$ = partial molar property change of mixing.

← come from

$$\bar{V}_i = \left(\frac{\partial \bar{G}_i}{\partial P} \right)_{T,x} \qquad -\bar{S}_i = \left(\frac{\partial \bar{G}_i}{\partial T} \right)_{P,x}$$

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

These equations indicate the important role that the ratio $\hat{a}_i$ plays in solution thermodynamics. It is clear also that values of the property changes of mixing depend on the choice of the standard states.

† These equations have two uses. First, they provide approximate values for $\hat{f}_i$ when applied to appropriate composition ranges. Second, they provide reference values to which actual values of $\hat{f}_i$ may be compared.

EQUATIONS

$$\hat{a}_{i,id} = x_i$$

$$\frac{\Delta G^{id}}{RT} = \sum x_i \ln x_i \qquad \frac{\Delta S^{id}}{R} = -\sum x_i \ln x_i$$

$$M^E = M - M^{id} \qquad M^E = \Delta M^E$$
$$\Delta M^E = \Delta M - \Delta M^{id}$$

$$\overline{M}_i^E = \overline{M}_i - \overline{M}_i^{id}$$

$$\frac{G^E}{RT} = \sum x_i \ln \gamma_i \qquad \gamma_i \equiv \frac{\hat{f}_i}{x_i f_i^o} = \frac{\hat{f}_i}{\hat{f}_i^{ip}}$$

$$\ln \gamma_i = \frac{\overline{G}_i^E}{RT} = \left[\frac{\partial (n G^E/RT)}{\partial n_i}\right]_{T,P,n_j}$$

G^E, $\ln \gamma_i$ depend on the standard state

ASSUMPTIONS, RESTRICTIONS

- IDEAL SOLUTION & GASES!

EQUATIONS

- $dU^T + PdV^T - TdS^T \leq 0$
- $(dG^T)_{TP} \leq 0$ (constant T, P)

DEFN The equilibrium state of a closed system is that state for which the total Gibbs free energy is a minimum w/respect to all possible changes at the given T & P.

- $(dG^T)_{T,P} = 0$
- $\mu_i^\alpha = \mu_i^\beta = \cdots = \mu_i^\pi$
- $\hat{f}_i^\alpha = \hat{f}_i^\beta = \cdots = \hat{f}_i^\pi$

Phase Rule

$$F = 2 - \pi + N$$

Duhem's Theorem

- For any closed system formed initially from given masses of particular chemical species the equilibrium state is COMPLETELY DETERMINED when any 2 independent variables are fixed.

Vapor-Liquid Equilibrium

$$\left.\begin{aligned} \hat{f}_i^V &= \hat{\phi}_i^V y_i P \\ \hat{f}_i^L &= \hat{\phi}_i^L x_i P \end{aligned}\right\} \text{defns.} \rightarrow y_i \hat{\phi}_i^V = x_i \hat{\phi}_i^L$$

ASSUMPTIONS, RESTRICTIONS

- MUST be SATISFIED FOR CHANGES IN STATE OF ANY CLOSED SYSTEM OF UNIFORM T & P
- (<) corresponds to incremental changes in nonequilibrium states.
- (=) corresponds to incremental changes between equilibrium states (reversible)

- for systems already at equilibrium.
- derived from fundamental property relation.
- derived from $d\mu_i = RT d\ln \hat{f}_i$

- π = # of phases
- N = # of species

- we generally fix T, P, and either liquid phase or vapor phase compositions.
- remember, $\hat{\phi}_i = f(x_i, T, P)$

EQUATIONS

ASSUMPTIONS, RESTRICTIONS

DERIVATION of RAOULT'S LAW

1) $\hat{\Phi}_i^V = 1$
2) $\hat{\phi}_i^L = \frac{f_i^L}{P}$
3) $f_i^L \neq f(P)$

$$y_i = \frac{x_i P_i^{SAT}}{P}$$

- ideal gas
- ideal solution ⊂ ∀ major league
- liquid fugacity is not a function of P.

- the failure of Raoult's law is due to differences in molecular size and in the molecular force fields of the components.
- liquid phase non-idealities are of primary importance
- at high P, deviations from ideal gas must also be considered

- At the molecular level, appreciable negative deviations from Raoult's law reflect stronger intermolecular forces between unlike than between like pairs of molecules. Conversely, appreciable positive deviations result for solutions in which intermolecular forces between like molecules are stronger than between unlike. In this latter case, the forces between like molecules may be so strong in comparison w/those between unlike molecules as to prevent complete miscibility.

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

- FROM DEFN of γ_i

$y_i \hat{\Phi}_i P = x_i \gamma_i f_i^\circ$

- VLE equation

LOW to MODERATE PRESSURES

$y_i \hat{\Phi}_i P = x_i \gamma_i \Phi_i^{SAT} P_i^{SAT}$

1) γ_i, f_i° are independent of P ($f_i^\circ = \Phi_i^{SAT} P_i^{SAT}$)
- Φ_i^{SAT} found from vapor phase EOS.
- $\ln\gamma_i$ found from $\left[\frac{\partial(nG^E/RT)}{\partial n_i}\right]_{T,P,n_i}$
- need G^E/RT as $f(T, x_i)$ (since $\gamma_i \neq f(P)$)

$$\ln\gamma_i = 1 - \ln\left(\sum_j x_j G_{ij}\right) - \sum_k \left(\frac{x_k G_{ki}}{\sum_j x_j G_{kj}}\right)$$ Wilson correlation

$$G_{ij} = \frac{V_j}{V_i} \exp\left[\frac{-a_{ij}}{RT}\right]$$ a_{ij} = constant

EQUATIONS

High Pressures

$\gamma_i = \delta(P, T, x_i)$ and vapor phase properties are not represented well by using 2-term virial eqn.

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i f_i^\circ}{\hat{\phi}_i P} \qquad K = \delta(T, P, y_i, x_i)$$

$$K_i = \frac{\gamma_i \phi_i^\ell}{\hat{\phi}_i^v}$$

- ϕ_i^ℓ found from Pitzer correlation
- $\hat{\phi}_i^v$ " " Redlich-Kwong EOS
- γ_i " " Scatchard-Hildebrand

$$\ln \gamma_i = \frac{V_i}{RT}(\delta_i - \bar{\delta})^2 \qquad \delta = \frac{\sum_K (x_K V_K \delta_K)}{\sum_K (x_K V_K)}$$

$$\delta_i = \left(\frac{\Delta U_i^{VAP}}{V_i}\right)^{1/2}$$

Activity Coefficients

$$\frac{G^E/RT}{x_1 x_2} = B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \ldots$$

$$\frac{G^E/RT}{x_1 x_2} = A_{21} x_1 + A_{12} x_2$$

$$\ln \gamma_1 = x_2^2 [A_{12} + 2(A_{21} - A_{12}) x_1]$$
$$\ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21}) x_2]$$

$$\frac{G^E/RT}{x_1 x_2} = \frac{A_{12}' A_{21}'}{A_{12}' x_1 + A_{21}' x_2}$$

Assumptions, Restrictions

- assumes $f_i^\circ = f_i^L$ at T, P of system
- regular solution theory

- generally correlated around $\frac{G^E}{RT}$.
- REDLICH-KISTER
  - ✓ $\ln \gamma_1^\infty = B = \ln \gamma_2^\infty$
- Margules
  - ✓ $\ln \gamma_1^\infty = A_{12}$
  - ✓ $\ln \gamma_2^\infty = A_{21}$
- VAN LAAR
  - ✓ $\ln \gamma_1^\infty = A_{12}'$
  - ✓ $\ln \gamma_2^\infty = A_{21}'$

- The two constants in the van Laar, Margules, and Wilson eqns can be found from numerical regression.

EQUATIONS	ASSUMPTIONS, RESTRICTIONS
$d\left(\frac{G^E}{RT}\right) = -\frac{\Delta H}{RT^2}dT$, $d\ln\gamma_i = -\frac{\overline{\Delta H}_i}{RT^2}dT$	• If heat of mixing data are available, these equations can be integrated over a temperature interval, allowing values of G^E/RT and $\ln\gamma_i$ to be calculated at one T from given values at another T.
$-\frac{\Delta H}{RT^2}dT + \frac{\Delta V}{RT}dP = \Sigma x_i\, d\ln\gamma_i$	• applies to any phase; imposing a constraint on how the activity coefficients of the components in the phase may vary w/ T, P or x_i. • derived from Gibbs Duhem applied to G^E/RT.
$x_1\frac{d\ln\gamma_1}{dx_1} + x_2\frac{d\ln\gamma_2}{dx_1} = 0$	• derived from Gibbs Duhem when $\Delta H, \Delta V_{mix} = 0$ • CONSTANT T or P, ~~liquid~~ gas
$x_1\frac{d\ln y_1P}{dx_1} + x_2\frac{d\ln y_2P}{dx_1} = 0$	• good for const T, binary, low pressure • form of Gibbs-Duhem • used as a thermo check of data.
$\Downarrow$ $\frac{dP}{dy_1} = \frac{P(y_1 - x_1)}{y_1(1-y_1)}$ COEXISTENCE EQUATION	• follows directly from Gibbs-Duhem for a binary system and must be satisfied whenever 2 phases coexist in equil at constant T and low P, • used as a thermo check of data
$\gamma_1^\infty \simeq \frac{1}{P_1^{SAT}}\left[\frac{P - P_2^{SAT}}{x_1} + P_2^{SAT}\right]$ $\gamma_2^\infty \simeq \frac{1}{P_2^{SAT}}\left[\frac{P - P_1^{SAT}}{x_2} + P_1^{SAT}\right]$	• ideal gas, • derived from coexistence equation.

ideal gas

Equations

Assumptions, Restrictions

Stability

$\Delta G_{mix} < 0$

- const T, P, 2 liquids mix
- follows from eqn #2.

Stability criterion for a single-phase binary system

1) at const T, P, ΔG and its 1ST & 2ND derivatives must be continuous functions in x_1

2) $\frac{d^2(\Delta G/RT)}{dx_1^2} > 0$

- const T, P

3) $\frac{d^2(\Delta G/RT)}{dx_1^2} = \frac{1}{x_1}\frac{d\ln \hat{f}_2}{dx_2}$

4) $\frac{d^2(\Delta G/RT)}{dx_1^2} = \frac{1}{x_2}\frac{d\ln \hat{f}_1}{dx_1}$

- for a stable phase, the fugacity of each component in a binary system always increases as its mole fraction increases at const T & P.

or

$\frac{d(y_1 P)}{dx_1} > 0 \;;\; \frac{d(y_2 P)}{dx_1} < 0 \;;\; \frac{dy_1}{dx_1} > 0$

- const T, low P, ideal gas, binary system.

$\frac{dP}{dx_1}$, $\frac{dP}{dy_1}$ and $(y_1 - x_1)$ must have the same sign.

EQUATIONS

$\nu_1 A_1 + \nu_2 A_2 + \cdots \nu_N A_N = 0$

$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \cdots \frac{dn_N}{\nu_N} = d\varepsilon \quad \Rightarrow dn_i = \nu_i d\varepsilon$

$dn_i = \sum_j \nu_{ij} d\varepsilon_j$

$(dG^t)_{T,P} = 0$ at equilibrium

also, $\sum \nu_i \mu_i = 0$ at equilibrium

\# $K = \prod \hat{q}_i^{\nu_i} \qquad \hat{q}_i = \hat{S}_i / S_i^\circ$ (4)

- comes from $\sum \nu_i \mu_i = 0$ and $\mu_i = G_i^\circ + RT \ln \hat{q}_i$

$-RT \ln K = \sum \nu_i G_i^\circ \equiv \Delta G^\circ$

- for gas, standard state is usually ideal gas state of pure i at 1 atm

$K = \prod \hat{f}_i^{\nu_i}$

- for solid & liq, stand. state is the pure solid & liq at 1 atm & T

ΔG° is fixed at a certain temperature & is indep of P & x_i

$\Delta M^\circ = \sum \nu_i M_i^\circ$

$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$ comes from $\frac{d(\Delta G/RT)}{dT} = \frac{\Delta H^\circ}{RT^2}$

ASSUMPTIONS & RESTRICTIONS

ν = + for product
= − for reactant

ε = ant. of reaction
= reaction coordinate or extent

for j reactions.

- comes from total differential of Gibbs free energy of a single-phase multi-component system.

ΔG° is called the standard Gibbs energy change of reaction.

- only good for GAS PHASE

- standard property changes of reaction
- gives the effect of T on the K.

\# Provides the connection between the equilibrium state and the standard state of the constituents. Standard state must be at the equilibrium temperature T.

Eqns.

ASSUMPTIONS, RESTRICTIONS

$$\ln K = \frac{1}{R}\int \frac{\Delta H^\circ}{T^2}\,dT + I$$

- I, ΔH_o are constants of integration

$$\Delta H^\circ = \Delta H_o + \int \Delta C_p^\circ\,dT$$

3 ways to determine K

1) determine values of K from compositions ($K = \pi a^{\nu}$) at 2 T's.
- then use

$$\ln K = -\frac{\Delta H_o}{T} + \frac{\Delta\alpha}{R}\ln T + \frac{\Delta\beta}{2R}T + \frac{\Delta\gamma}{6R}T^2 + I = RT\Delta G^\circ$$

2) Determine ΔH_o from ΔH_{RXN}
- use one value of K and above eqn to get I

3) Determine ΔH_o from ΔH_{RXN}
Determine I from ΔG°

$$K = \pi \hat{f}_i^{\nu_i} \qquad K = f(T) \qquad \hat{f}_i = f(T, x_i, P)$$

- GAS PHASE

$$\pi (y_i \hat{\phi}_i)^{\nu_i} = P^{-\nu} K \qquad \nu = \Sigma \nu_i$$

$$\pi (y_i \phi_i)^{\nu_i} = P^{-\nu} K$$

- ideal solution

$$\pi (y_i)^{\nu_i} = P^{-\nu} K$$

- ideal gas ($P\downarrow, T\uparrow$)

$$K = \pi (x_i \gamma_i)^{\nu_i} \qquad \leftarrow \text{Liquids}$$

- assumes $\frac{f_i}{f_i^\circ} = 1$ for liquid.

$$* \exp\left[\frac{P-1}{RT}\Sigma \nu_i V_i\right]$$

- correction for real fluids.

EQUATIONS

$K = \prod x_i^{\nu_i}$ LAW of MASS ACTION

$\hat{a}_i = x_i$

$\hat{a}_i = m_i$ molality

Phase Rule

$F = 2 - \pi + N - r$

ASSUMPTIONS, RESTRICTIONS

- IDEAL LIQUID SOLUTION, $\gamma_i = 1$
- mean. pure species concentration
- in very dilute solution

π = # of phases
N = # of species
r = # of reactions