
Thermodynamics

Check Point

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Fundamentals

→ **Microscopic vs. Macroscopic View Point**

→ **State function vs. Process variable**

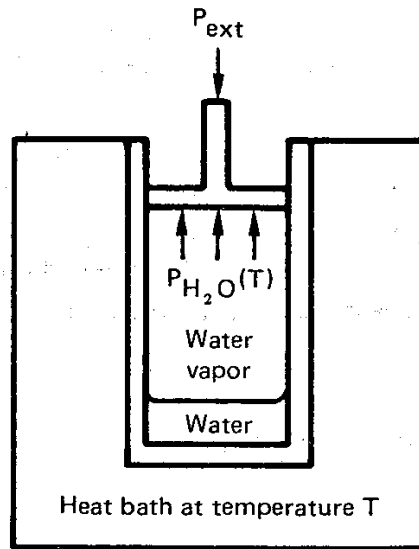
→ **First Law of Thermodynamics**

→ **Special processes**

1. *Constant-Volume Process: $\Delta U = q_v$*
2. *Constant-Pressure Process: $\Delta H = q_p$*
3. *Reversible Adiabatic Process: $q = 0$*
4. *Reversible Isothermal Process: $\Delta U = \Delta H = 0$*



Second Law of thermodynamics - Reversible vs. Irreversible



$$\begin{aligned}\Delta S &= \text{measurable quantity} + \text{un-measurable quantity} \\ &= q/T + \Delta S_{\text{irr}} \\ &= q_{\text{rev}}/T\end{aligned}$$



Second Law of thermodynamics - Maximum Work

$$U_B - U_A = q - w$$

$$\delta q = dU_{\text{system}} + \delta w$$

$$dS_{\text{system}} = \frac{\delta q}{T} + dS_{\text{irr}}$$

$$dS_{\text{system}} = \frac{dU_{\text{system}} + \delta w}{T} + dS_{\text{irr}}$$

$$\delta w = TdS_{\text{system}} - dU_{\text{system}} - TdS_{\text{irr}}$$

$$w \leq w_{\text{max}} = T\Delta S_{\text{system}} - \Delta U_{\text{system}}$$



Second Law of thermodynamics - Entropy as a Criterion of Equilibrium

※ for an isolated system of constant U and constant V ,
(adiabatically contained system of constant volume)
equilibrium is attained when the entropy of the system is maximum.

※ for a closed system which does no work other than work of
volume expansion,

$$dU = T dS - P dV \quad (\text{valid for reversible process})$$

U is thus the natural choice of dependent variable for S and V
as the independent variables.

※ for a system of constant entropy and volume, equilibrium is attained
when the internal energy is minimized.

$$\delta w = TdS_{\text{system}} - dU_{\text{system}} - TdS_{\text{irr}}$$

$$PdV = TdS_{\text{system}} - dU_{\text{system}} - TdS_{\text{irr}}$$

$$0 = dU_{\text{system}} + TdS_{\text{irr}}$$



Second Law of thermodynamics - Condition for Thermodynamic Equilibrium

※ Further development of Classical Thermodynamics results from the fact that S and V are an inconvenient pair of independent variables.

+ need to include composition variables in any equation of state and in any criterion of equilibrium

+ need to deal with non P - V work
(e.g., electric work performed by a galvanic cell)

※ Condition for Thermodynamic Equilibrium of a Unary two phase system

$$\begin{aligned}dS_{isolated_system} &= dS^\alpha + dS^\beta \\ &= \left(\frac{1}{T^\alpha} - \frac{1}{T^\beta} \right) dU^\alpha + \left(\frac{P^\alpha}{T^\alpha} - \frac{P^\beta}{T^\beta} \right) dV^\alpha - \left(\frac{\mu^\alpha}{T^\alpha} - \frac{\mu^\beta}{T^\beta} \right) dn^\alpha\end{aligned}$$

The same conclusion is obtained using minimum internal energy criterion.



New Thermodynamic Functions – Reason for the necessity

- ❖ Further development of Classical Thermodynamics results from the fact that S and V are an inconvenient pair of independent variables.
 - + need to include composition variables in any equation of state and in any criterion of equilibrium
 - + need to deal with non P - V work (e.g., electric work performed by a galvanic cell)

$$dU = TdS - PdV$$

S , V are not easy to control. Need to find new state functions which are easy to control and can be used to estimate equilibrium

→ **F, G**



Helmholtz Free Energy - Work Function, $F \equiv U - ST$

$$dF \equiv dU - TdS - SdT$$

For a reversible process

$$dF = [TdS - PdV - \delta w'] - TdS - SdT = -SdT - PdV - \delta w'$$

$$dF_T = -PdV - \delta w' = -\delta w_{T.Total}$$

- ▷ Maximum work that the system can do by changing its state at Constant T, V
 $= -\Delta F$.

For an irreversible isothermal process

$$\Delta F_T = [q - w] - T\Delta S$$

$$T\Delta S = q + T\Delta S_{irr}$$

$$w = P\Delta V + w' = w' \quad \text{For constant } V$$

$$\Delta F_{T,V} + w' + T\Delta S_{irr} = 0$$

- ▷ If cannot do a maximum work, it's due to the creation of Δs_{irr} .
Under a Constant T, V , an equilibrium is obtained when the system has maximum $(w' + T\Delta s_{irr})$ or minimum F .



Helmholtz Free Energy - Example

Equilibrium between condensed phase and gas phase.

Use Helmholtz Free Energy Criterion to determine equilibrium amount of gaseous phase at a given temperature, and how it changes with changing temperature

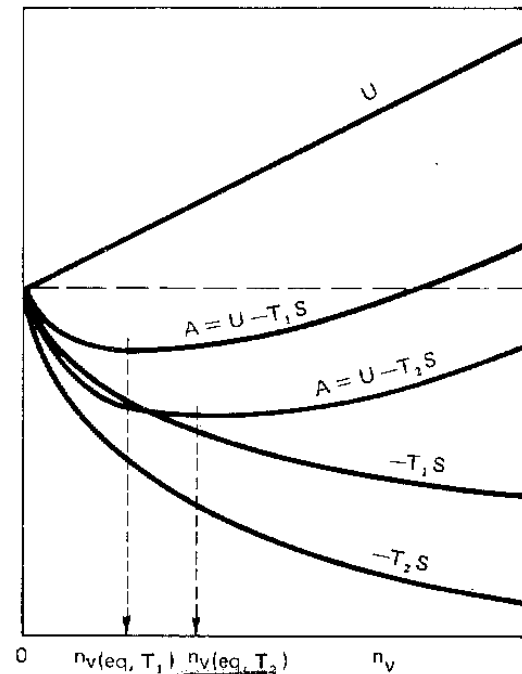


Fig. 5.3. The effect of temperature on the equilibrium state of a closed solid-vapor system of constant volume.



Gibbs Free Energy - Gibbs Function, $G \equiv U + PV - ST$

$$dG \equiv dU + PdV + VdP - TdS - SdT$$

For a reversible process

$$dG = [TdS - PdV - \delta w'] + PdV + VdP - TdS - SdT = -SdT + VdP - \delta w'$$
$$dG_{T,P} = -\delta w'$$

▷ Maximum work that the system can do by changing its state at Constant T, P
 $= -\Delta G$.

For an irreversible isothermal process

$$\Delta G_{T,P} = [q - w] + P\Delta V - T\Delta S$$
$$T\Delta S = q + T\Delta S_{irr}$$
$$w = P\Delta V + w'$$

$$\Delta G_{T,P} + w' + T\Delta S_{irr} = 0$$

▷ If cannot do a maximum work, it's due to the creation of Δs_{irr} .
Under a Constant T, P , an equilibrium is obtained when the system has
maximum ($w' + T\Delta s_{irr}$) or minimum G .



Thermodynamic Relations - For a closed system

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dF = -SdT - PdV$$

$$dG = -SdT + VdP$$



Thermodynamic Relations - For a multicomponent system

$$\triangleright G = G(T, P, n_i, n_j, n_k, \dots)$$

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P, n_i, n_j, \dots} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_i, n_j, \dots} dP + \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j, n_k, \dots} dn_i + \left(\frac{\partial G}{\partial n_j} \right)_{T, P, n_i, n_k, \dots} dn_j + \dots$$

$$\triangleright \text{Chemical Potential} \quad \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j, n_k, \dots} \equiv \mu_i$$

$$dG = -SdT + VdP + \sum_1^n \mu_i dn_i$$

$$\delta w = PdV - \sum \mu_i dn_i$$

$-\sum \mu_i dn_i$ is the chemical work done by the system



Gibbs Energy for a Unary System - from $dG = -SdT + VdP$

Gibbs Energy as a function of T and P

$$dG = -S dT + V dP$$

$$G(T, P) - G(T_o, P_o) = -\int_{T_o}^T S dT + \int_{P_o}^P V dP$$

@ constant P

$$S(T) = S_o + \int_{T_o}^T \frac{C_P(T)}{T} dT$$

$$G(T) = G(T_o) - \int_{T_o}^T \left[S_o + \int_{T_o}^T \frac{C_P(T)}{T} dT \right] dT$$

@ constant T

$$G(P) - G(P_o) = \int_{P_o}^P V dP$$



Gibbs Energy for a Unary System - from $G = H - ST$

Gibbs Energy as a function of T and P

$$G = H - ST$$

$$\begin{aligned} G(T, P) &= (H(T, P) - H(T_o, 1)) + H_o - (S(T, P) - S(T_o, 1) + S_o)T \\ &= \Delta H + H_o - (\Delta S + S_o)T = H_o - S_o T + \Delta H - T\Delta S \end{aligned}$$

@ constant P

$$H(T) = H_o + \int_{T_o}^T C_P(T) dT \quad S(T) = S_o + \int_{T_o}^T \frac{C_P(T)}{T} dT$$

$$G(T) = H_o - S_o T + \int_{T_o}^T C_P(T) dT - T \int_{T_o}^T \frac{C_P(T)}{T} dT$$

@ constant T

$$\Delta H = \int_{P_o}^P \left(\frac{\partial H}{\partial P} \right)_T dP = \int_{P_o}^P \left[T \left(\frac{\partial S}{\partial P} \right)_T + V \right] dP = \int_{P_o}^P \left[-T \left(\frac{\partial V}{\partial T} \right)_T + V \right] dP = \int_{P_o}^P V(1 - \alpha T) dP$$

$$\Delta S = \int_{P_o}^P \left(\frac{\partial S}{\partial P} \right)_T dP = - \int_{P_o}^P \left(\frac{\partial V}{\partial T} \right)_T dP = - \int_{P_o}^P \alpha V dP$$



Gibbs Energy for a Unary System - Temperature Dependency

$$G(T) = G(T_o) - \int_{T_o}^T \left[S_o + \int_{T_o}^T \frac{C_P(T)}{T} dT \right] dT$$

$$G(T) = H_o - S_o T + \int_{T_o}^T C_P(T) dT - T \int_{T_o}^T \frac{C_P(T)}{T} dT$$

서로 다른 출발점에서 유도된 위의 두 식은 같은 식인가?

Empirical Representation of Heat Capacities $c_p = a + bT + cT^{-2}$

를 이용하여 위의 두 식이 동일한 것임을 증명하라.



Gibbs Energy for a Unary System

$$G(T) = H_o - S_o T + \int_{T_o}^T C_P(T) dT - T \int_{T_o}^T \frac{C_P(T)}{T} dT + \int_{P_o}^P V dP$$

- $V(T,P)$ based on expansivity and compressibility
- $C_p(T)$
- S_{298} : by integrating C_p/T from 0 to 298 K and using 3rd law of thermodynamics (the entropy of any homogeneous substance in complete internal equilibrium may be taken as zero at 0 K)
- H_{298} : from first principles calculations, but generally unknown
- ※ H_{298} becomes a reference value for G_T
- ※ Introduction of Standard State



Criterion of Thermodynamic Equilibrium, Thermodynamic Relations

- Helmholtz Free Energy, Gibbs Free Energy
- Correlation btw Free energy minimum & equilibrium
- Chemical Potential vs. Gibbs energy
- $-\sum \mu_i dn_i$ Term as a Chemical Work
- Thermodynamic Relations: Importance & Applications



Statistical Thermodynamics

- **Basic Concept of Statistical Thermodynamics**
- **Application of Statistical Thermodynamics to Ideal Gas**
- **Understanding Entropy through the Concept of the Statistical Thermodynamics**
- **Heat capacity**
- **Heat capacity at low temperature**



Application of Criterion

1.1기압 하 Pb의 melting point 는 600K이다.

1기압 하 590K로 과냉된 액상 Pb가 응고하는 것은
자발적인 반응이라는 것을

(1) maximum-entropy criterion과

(2) minimum-Gibbs-Energy criterion을 이용하여 보이시오.

$$\Delta H_{melting} = 4810 \text{ J / mole}$$

$$C_{p(l)} = 32.4 - 3.1 \times 10^{-3} T \text{ J / mol} \cdot K$$

$$C_{p(s)} = 9.75 \times 10^{-3} T \text{ J / mol} \cdot K$$

2. 1번 문제에서의 Pb가 단열된 용기에 보관되어 있었다면
용기 내부는 결국 어떠한 (평형)상태가 될 것인지 예측하시오.



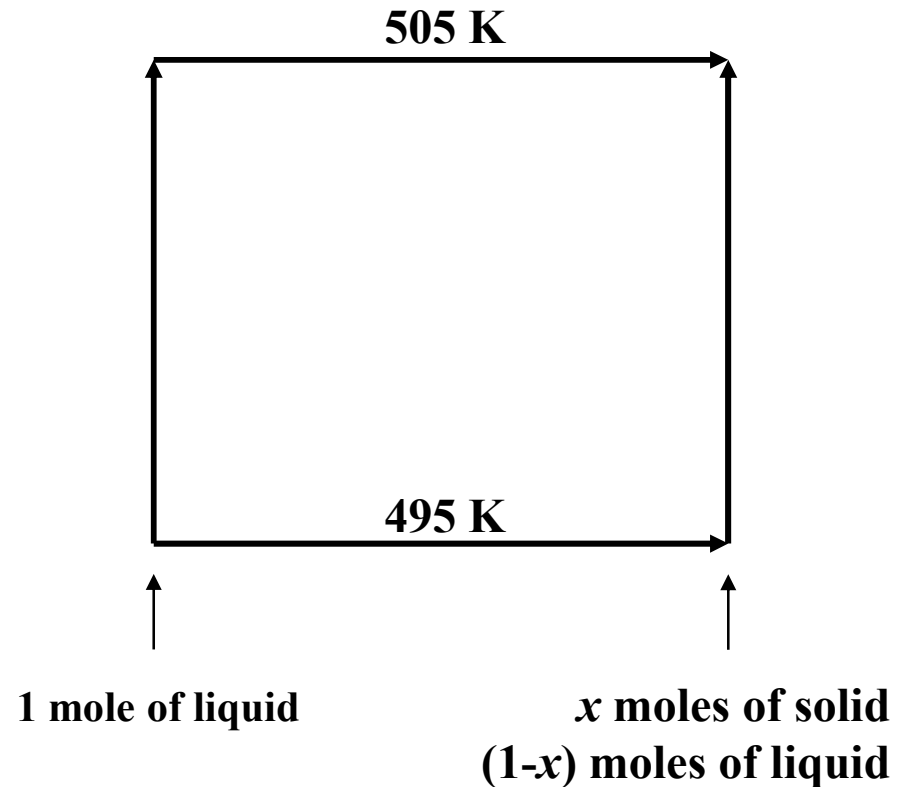
Numerical Example

- A quantity of supercooled liquid Tin is adiabatically contained at 495 K. Calculate the fraction of the Tin which spontaneously freezes. Given

$$\Delta H_m^{Sn} = 7070 \text{ J at } T_m = 505 \text{ K}$$

$$C_{p,Sn(l)} = 34.7 - 9.2 \times 10^{-3} T \text{ J/K}$$

$$C_{p,Sn(s)} = 18.5 + 26 \times 10^{-3} T \text{ J/K}$$



Thermodynamics

Phase Equilibria in a One-Component System

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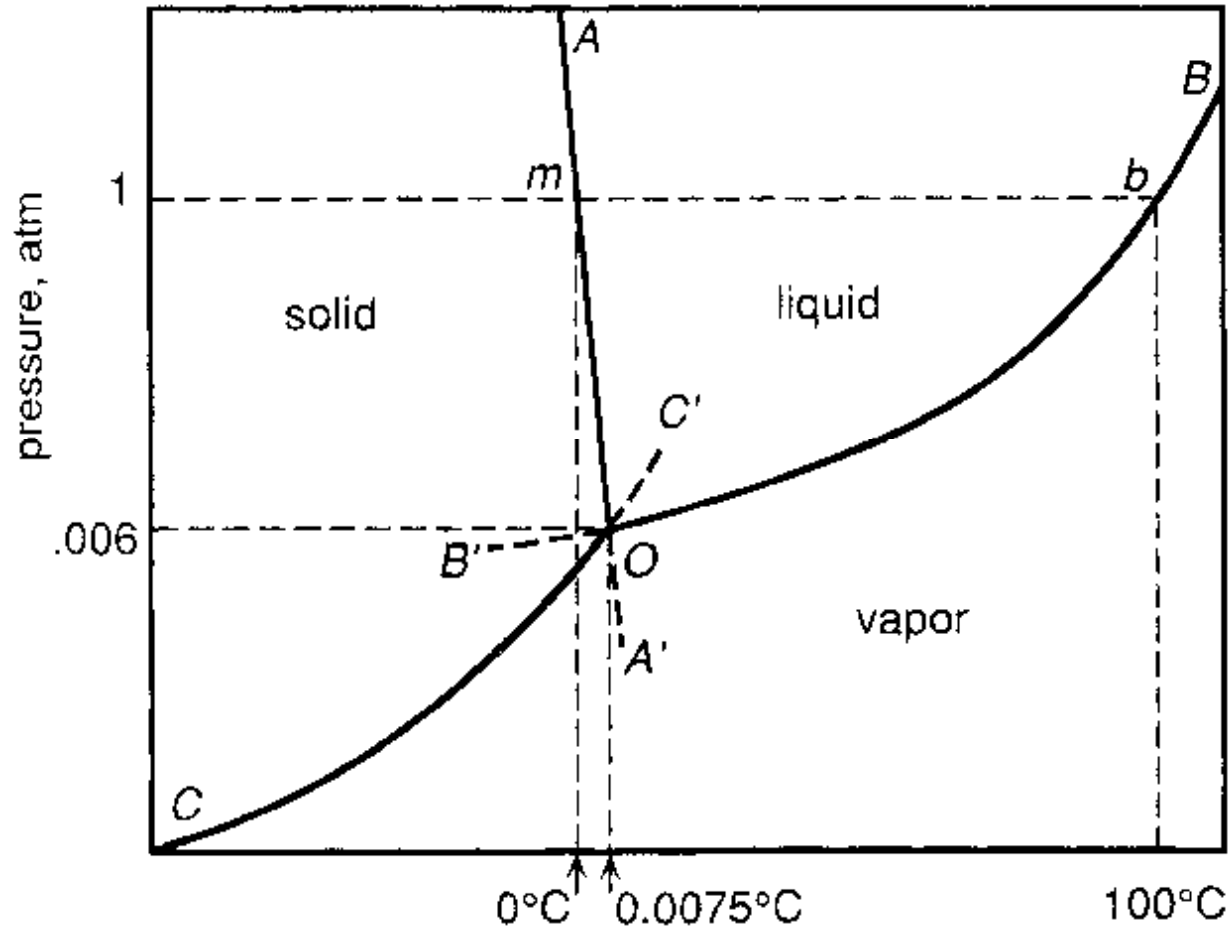
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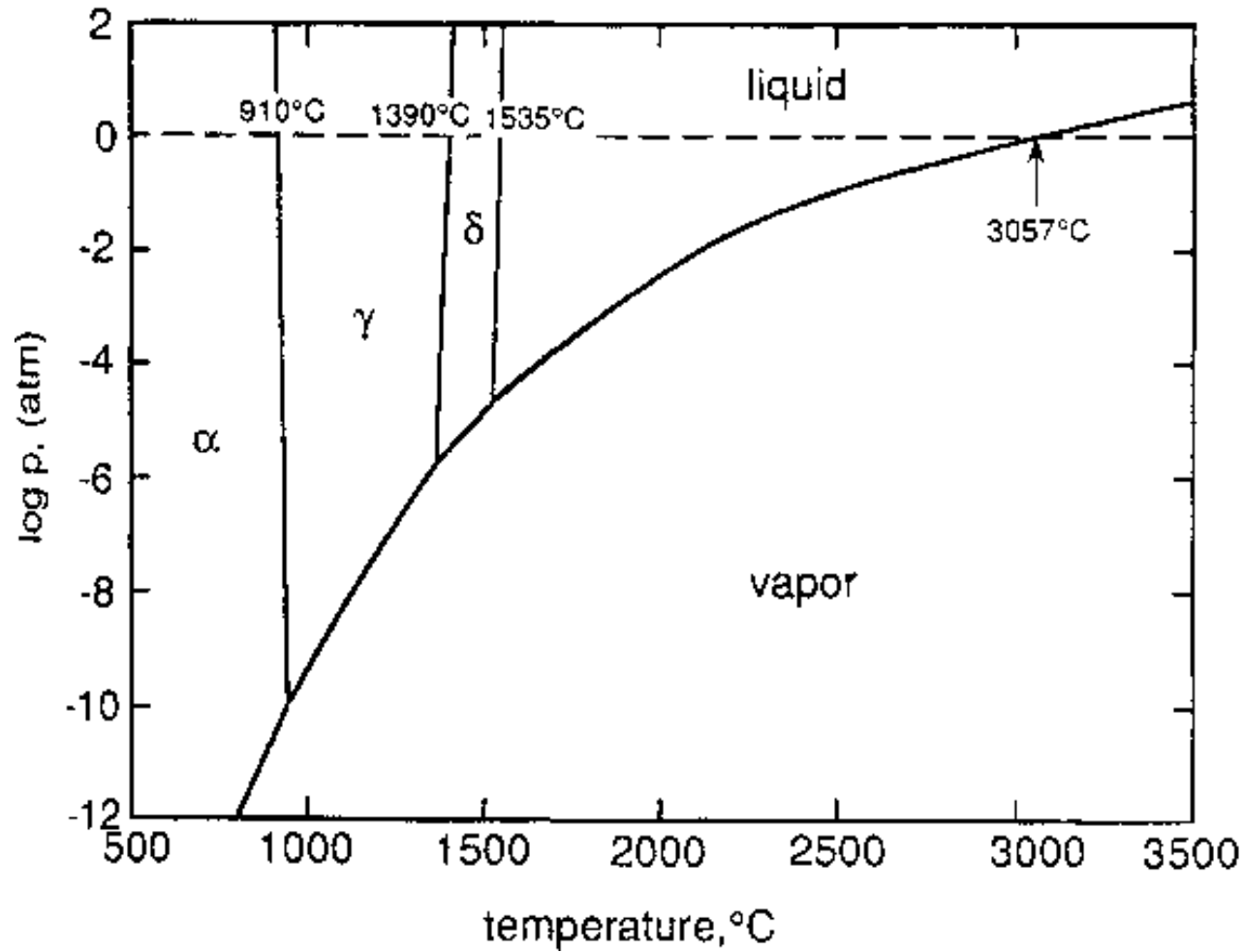
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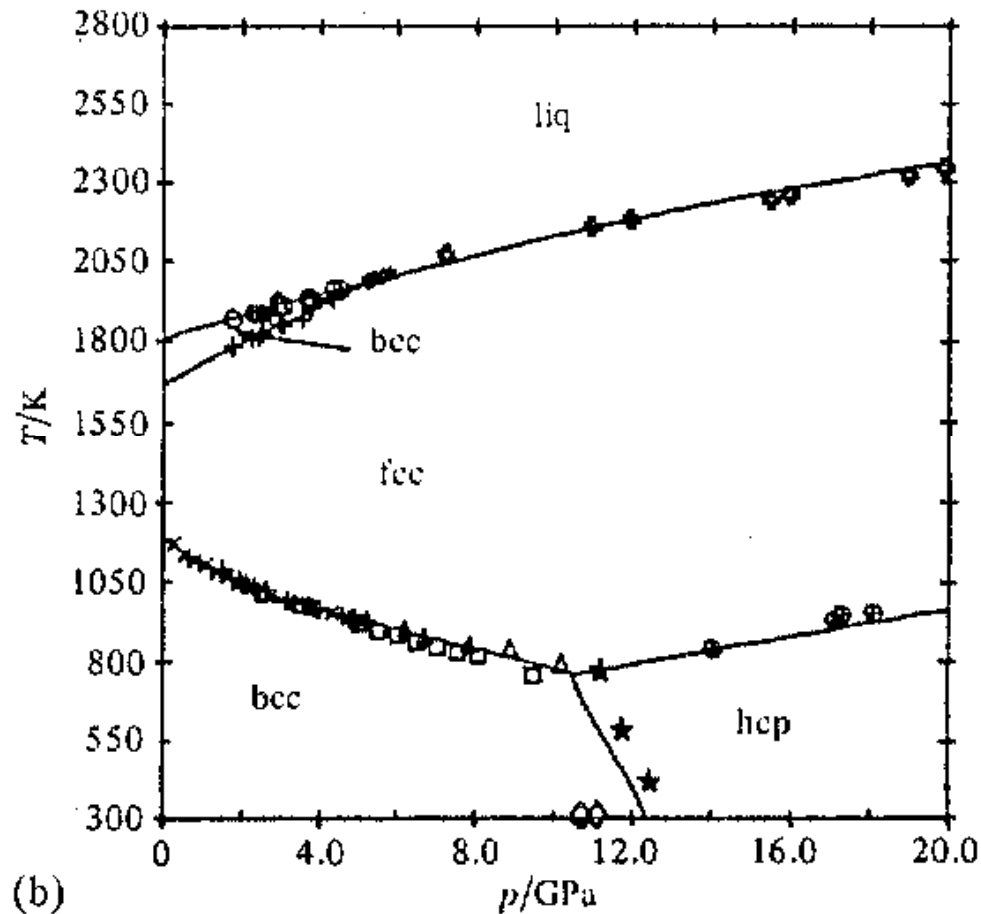
Phase Diagram for H₂O



Phase Diagram for Fe



Phase Diagram for Fe



- bcc/fcc
 - × Kennedy and Newton (1963)
 - Kaufman et al (1963)
 - △ Bundy (1965)
 - + Strong et al (1973)
- bcc/hcp
 - ★ Bundy (1965)
 - ◇ Mii et al (1970)
 - ◊ Giles et al (1971)
- bcc/liq
 - Strong et al (1973)
 - △ Liu and Bassett (1975)
- fcc/hcp
 - Bundy (1965)
- fcc/liq
 - * Strong et al (1973)
 - ◆ Liu and Bassett (1975)



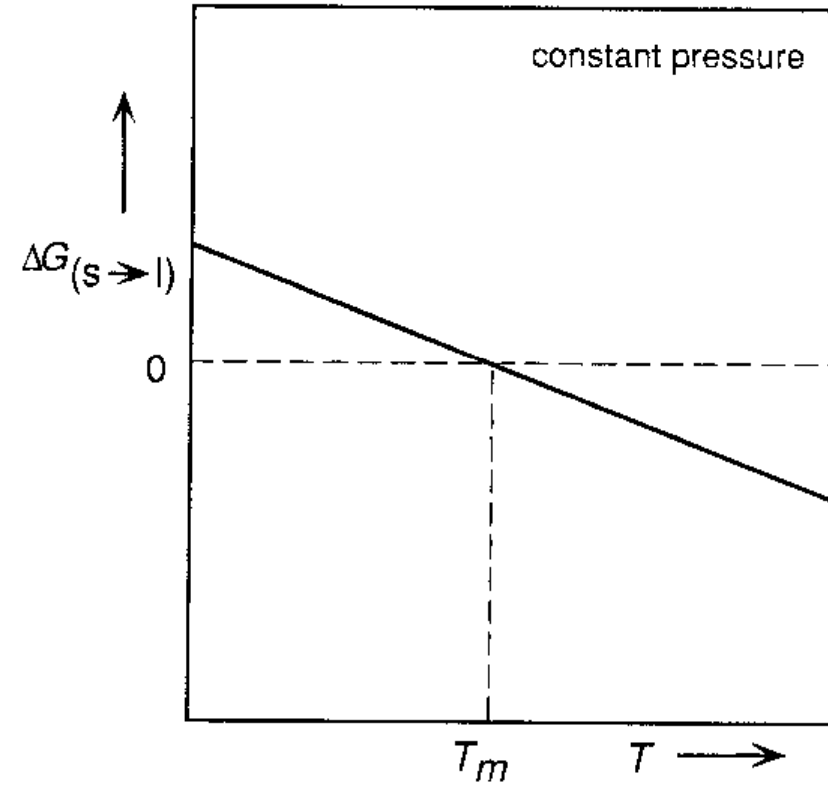
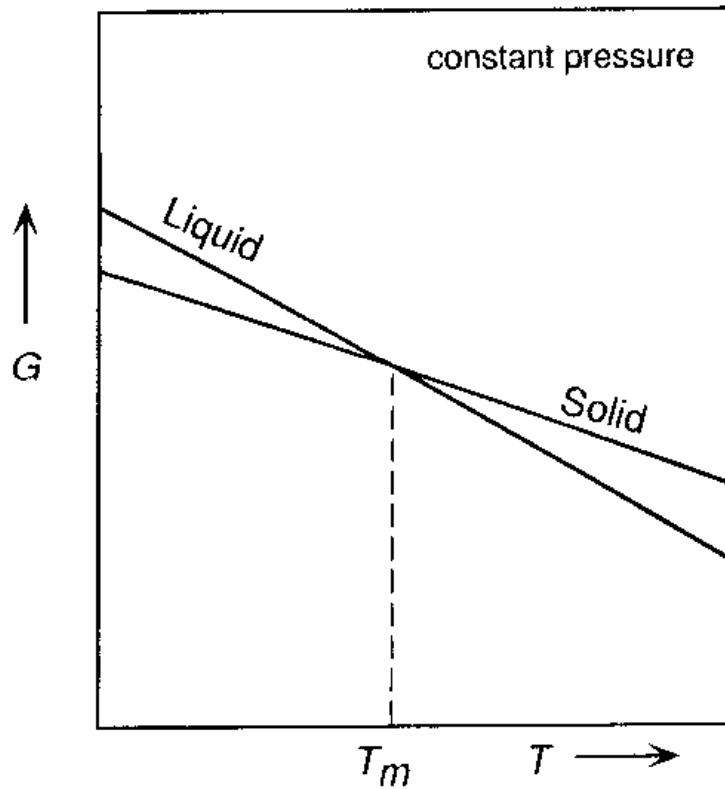
Equilibrium

- **Thermal, Mechanical and Chemical Equilibrium**
- **Concept of Chemical Potential**
 - In a one component system, $G_i = \mu_i$
- **Temperature and Pressure dependence of Gibbs free energy**

$$G(T) = H_o - S_o T + \int_{T_o}^T C_P(T) dT - T \int_{T_o}^T \frac{C_P(T)}{T} dT$$



Temperature Dependence of Gibbs Energy



Temperature Dependence of Gibbs Energy - for H₂O

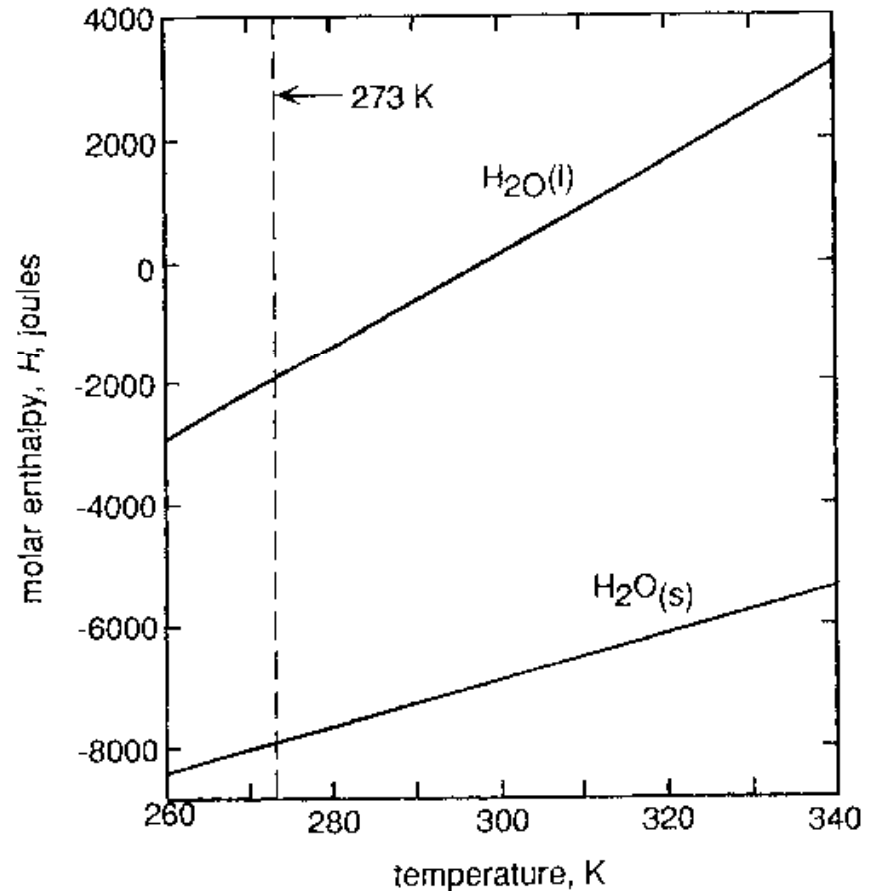
$$\Delta H_m = \Delta H_{(s \rightarrow l)} = 6008 \text{ J at } 273\text{K}$$

$$S_{H_2O(l), 298\text{K}} = 70.08 \text{ J/K}$$

$$S_{H_2O(s), 298\text{K}} = 44.77 \text{ J/K}$$

$$C_{p, H_2O(l)} = 75.44 \text{ J/K}$$

$$C_{p, H_2O(s)} = 38 \text{ J/K}$$



Temperature & Pressure Dependence of Gibbs Energy

● Clausius-Clapeyron equation $\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T \Delta V}$

- For equilibrium between the vapor phase and a condensed phase

$$\Delta V = V_{\text{vapor}} - V_{\text{condensed-phase}} = V_{\text{vapor}} \quad \left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T V_v} = \frac{P \Delta H}{RT^2}$$

$$\frac{dP}{P} = \frac{\Delta H}{RT^2} dT \quad d \ln P = \frac{\Delta H}{RT^2} dT \quad \ln P = -\frac{\Delta H}{RT} + \text{constant}$$

$$\Delta H_T = \Delta H_{298} + \Delta C_P (T - 298) = [\Delta H_{298} - 298 \Delta C_P] + \Delta C_P \cdot T$$

$$\ln P = \left[\frac{298 \Delta C_P - \Delta H_{298}}{R} \right] \frac{1}{T} + \frac{\Delta C_P}{R} \ln T + \text{constant}$$



Phase Diagram - for H₂O

$$C_{p,H_2O(v)} = 30 + 10.7 \times 10^{-3} T + 0.33 \times 10^{-5} T^{-2} \text{ J / K}$$

$$C_{p,H_2O(l)} = 75.44 \text{ J / K}$$

$$\Delta C_{p(l \rightarrow v)} = -45.44 + 10.7 \times 10^{-3} T + 0.33 \times 10^{-5} T^{-2} \text{ J / K}$$

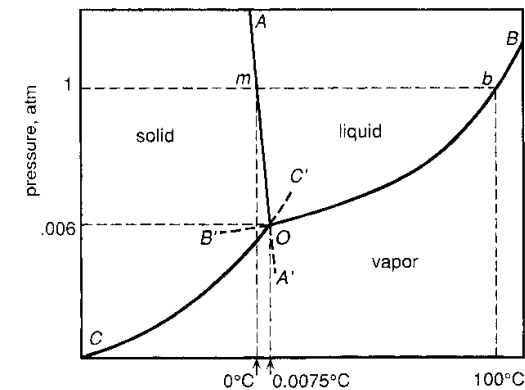
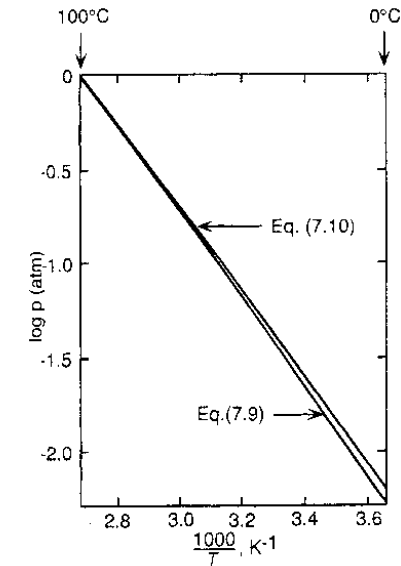
$$\Delta H_{evap,T} = \Delta H_{evap,373} + \int_{373}^T \Delta C_{p(l \rightarrow v)} dT$$

$$d \ln P = \frac{\Delta H}{RT^2} dT$$

$$\log P (\text{atm}) = -\frac{2,997}{T} - 5.465 \log T + 0.279 \times 10^{-3} T + \frac{862}{T^2} + 21.75$$

$$\log P (\text{atm}) = -\frac{2,900}{T} - 4.65 \log T + 19.732$$

● for S/L equilibrium $\left(\frac{dP}{dT} \right)_{eq} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T \Delta V}$



Equilibrium vapor pressures vs. Temperature

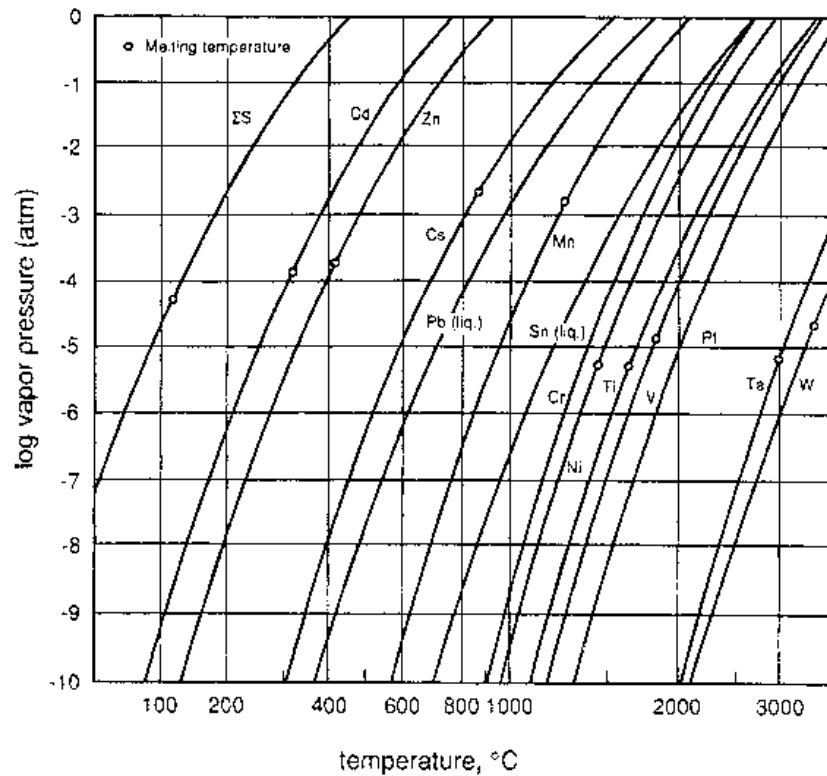


TABLE 3-1. Vapor pressures of elements: $\log(\text{Pa}/10^5\text{Pa})$.

Temp. K	Al(g)	Al ₂ (g)	Sb(g)	Sb ₂ (g)	Sb ₄ (g)	Be(g)	Be ₂ (g)
298.15	-50.643	-76.079	-39.313	-31.953	-27.403	-50.138	-101.832
500	-27.348	-41.694	-20.632	-15.652	-12.915	-27.210	-56.838
600	-21.629	-33.261	-16.045	-11.715	-9.426	-21.566	-45.814
700	-17.552	-27.253	-12.790	-8.915	-6.960	-17.538	-37.970
800	-14.502	-22.762	-10.341	-6.827	-5.138	-14.520	-32.113
900	-12.137	-19.282	-8.443	-5.219	-3.746	-12.177	-27.578
1000	-10.292	-16.591	-7.044	-4.168	-3.097	-10.305	-23.969
1100	-8.805	-14.436	-5.908	-3.328	-2.603	-8.776	-21.032
1200	-7.570	-12.649	-4.969	-2.638	-2.207	-7.506	-18.593
1300	-6.529	-11.145	-4.173	-2.063	-1.887	-6.433	-16.551
1400	-5.640	-9.862	-3.496	-1.577	-1.627	-5.517	-14.808
1500	-4.872	-8.775	-2.911	-1.163	-1.410	-4.725	-13.307
1600	-4.203	-7.792	-2.403	-0.806	-1.229	-4.051	-12.037
1700	-3.614	-6.947	-1.957	-0.496	-1.079	-3.472	-10.950
1800	-3.093	-6.200	-1.560	-0.224	-0.953	-2.958	-9.990
1900	-2.628	-5.535	-1.208	-0.080	-0.845	-2.500	-9.137
2000	-2.211	-4.939	-0.894	0.214	-0.753	-2.088	-8.374
ref.	1	1	3	3	3	1	1
Temp. K	Bi(g)	Bi ₂ (g)	Cd(g)	Ca(g)	Ca ₂ (g)	Cr(g)	Co(g)
298.15	-29.922	-30.192	-13.534	-25.232	-50.764	-61.765	-66.945
500	-15.126	-14.711	-5.659	-12.690	-26.715	-33.675	-36.779
600	-11.603	-11.148	-3.746	-9.623	-20.868	-26.775	-29.360
700	-9.167	-8.774	-2.464	-7.444	-16.734	-21.855	-24.066
800	-7.348	-7.012	-1.511	-5.828	-13.684	-18.172	-20.103
900	-5.937	-5.656	-0.775	-4.581	-11.347	-15.314	-17.026
1000	-4.818	-4.584	-0.193	-3.592	-9.505	-13.033	-14.569
1100	-3.897	-3.706	0.268	-2.794	-8.026	-11.172	-12.564
1200	-3.138	-2.990		-2.163	-6.872	-9.626	-10.898
1300	-2.497	-2.388		-1.639	-5.921	-8.323	-9.494
1400	-1.949	-1.877		-1.194	-5.119	-7.210	-8.297
1500	-1.474	-1.435		-0.812	-4.437	-6.250	-7.265
1600	-1.063	-1.055		-0.480	-3.850	-5.415	-6.365
1700	-0.697	-0.720		-0.191	-3.341	-4.682	-5.573
1800	-0.376	-0.427				-4.034	-4.879
1900	-0.090	-0.167				-3.458	-4.278
2000	0.155	0.047				-2.943	-3.738
ref.	3	3	3	1,4	1	1	1,5,6



Equilibrium vapor pressures vs. Temperature

Table A-4 The saturated vapor pressures of various substances $\left[\ln p \text{ (atm)} = -\frac{A}{T} + B \ln T + C \right]$

Substance	A	B	C	Range, K
$\text{CaF}_{2(s)}$	54,350	-4.525	56.57	298-1430
$\text{CaF}_{2(l)}$	53,780	-4.525	56.08	1430-1691 (T_m)
$\text{CaF}_{2(g)}$	50,200	-4.525	53.96	1691-2753 (T_b)
$\text{Fe}_{(l)}$	45,390	-1.27	23.93	1809 (T_m)-3330 (T_b)
$\text{Hg}_{(l)}$	7611	-0.795	17.168	298-630 (T_b)
$\text{Mn}_{(l)}$	33,440	-3.02	37.68	1517 (T_m)-2348 (T_b)
$\text{SiCl}_{4(l)}$	3620	—	10.96	273-333 (T_b)
$\text{Zn}_{(l)}$	15,205	-1.255	21.79	693 (T_m)-1177 (T_b)



Gibbs Phase Rule

- Degree of Freedom

number of variables which can be independently varied without upsetting the equilibrium

- $F = p(1+c) - (p-1)(2+c) = c - p + 2$



Example - Phase Transformation of Graphite to Diamond

- Calculate graphite→diamond transformation pressure at 298 K, given

$$H_{298,\text{gra}} - H_{298,\text{dia}} = -1900 \text{ J}$$

$$S_{298,\text{gra}} = 5.74 \text{ J/K}$$

$$S_{298,\text{dia}} = 2.37 \text{ J/K}$$

$$\text{density of graphite at 298 K} = 2.22 \text{ g/cm}^3$$

$$\text{density of diamond at 298 K} = 3.515 \text{ g/cm}^3$$

$$\Delta G = \Delta H - T\Delta S + \int_1^P \Delta V_{\text{graphite} \rightarrow \text{diamond}} dP$$



Thermodynamics

Multi-component Homogeneous System
Solution Thermodynamics

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Thermodynamic Properties of Gases - mixture of ideal gases

1 mole of ideal gas @ constant T:

$$dG = VdP = \frac{RT}{P} dP = RT d \ln P$$

$$G(P_2, T) - G(P_1, T) = RT \ln \frac{P_2}{P_1}$$

$$G(P, T) = {}^{\circ}G(T) + RT \ln P$$

$$G = {}^{\circ}G + RT \ln P$$

Mixture of Ideal Gases

- Definition of Mole fraction: x_i

$$p_i = x_i P$$

- Definition of partial pressure: p_i

- Partial molar quantities: $\bar{Q}_i = \left(\frac{\partial Q'}{\partial n_i} \right)_{T, P, n_j, n_k, \dots}$

$$\bar{G}_i = \mu_i$$

$$Q' = \sum n_i \bar{Q}_i \quad \left(\frac{\partial \bar{G}_i}{\partial P} \right)_{T, comp} = \bar{V}_i$$



Thermodynamic Properties of Gases - mixture of ideal gases

$$\bar{G}_i = {}^{\circ}G_i + RT \ln x_i + RT \ln P$$

Heat of Mixing of Ideal Gases

$$\frac{\partial(\bar{G}_i/T)}{\partial T} = \frac{\partial({}^{\circ}G_i/T)}{\partial T} \quad \bar{H}_i = {}^{\circ}H_i$$

$$\Delta H^{mix} = \sum_i n_i \bar{H}_i - \sum_i n_i {}^{\circ}H_i = 0$$

Gibbs Free Energy of Mixing of Ideal Gases

$$\Delta G^{mix} = \sum_i n_i \bar{G}_i - \sum_i n_i {}^{\circ}G_i = \sum_i n_i RT \ln x_i$$

Entropy of Mixing of Ideal Gases

$$\Delta G^{mix} = \Delta H^{mix} - T\Delta S^{mix} \quad \Delta S^{mix} = -\sum_i n_i R \ln x_i$$



Thermodynamic Properties of Gases - Treatment of nonideal gases

Introduction of fugacity, f

$$dG = RT d \ln f$$

$$\frac{f}{P} \rightarrow 1 \quad \text{as} \quad P \rightarrow 0$$

$$G = G^\circ + RT \ln f$$

For Equation of state $V = \frac{RT}{P} - \alpha$

$$V dP = RT d \ln f$$

$$d \ln \left(\frac{f}{P} \right) = -\frac{\alpha}{RT} dP$$

$$\ln \left(\frac{f}{P} \right)_{P=P} - \ln \left(\frac{f}{P} \right)_{P=0} = -\frac{\alpha P}{RT}$$

$$\frac{f}{P} = e^{-\alpha P / RT} \cong 1 - \frac{\alpha P}{RT} = \frac{PV}{RT} = \frac{P}{P_{id}}$$

- ※ actual pressure of the gas is the geometric mean of the fugacity and the ideal P
- ※ The percentage error involved in assuming the fugacity to be equal to the pressure is the same as the percentage departure from the ideal gas law



Thermodynamic Properties of Gases - Treatment of nonideal gases

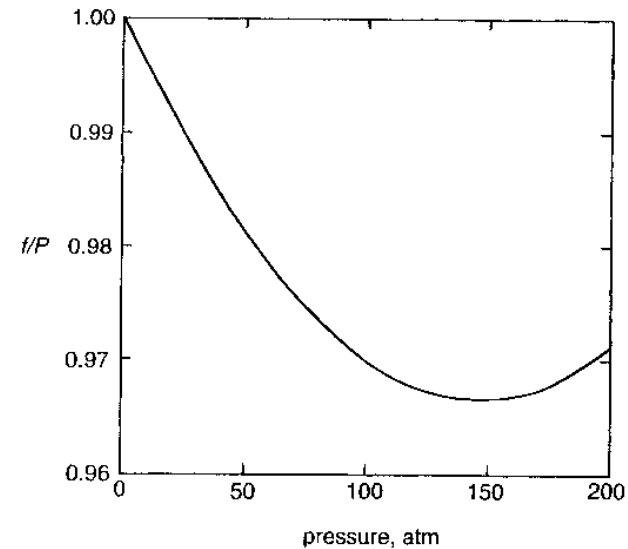
Alternatively,

$$d \ln \left(\frac{f}{P} \right) = -\frac{\alpha}{RT} dP = \left(\frac{V}{RT} - \frac{1}{P} \right) dP$$

$$Z \equiv \frac{PV}{RT} \qquad d \ln \left(\frac{f}{P} \right) = \frac{Z-1}{P} dP$$

$$\ln \left(\frac{f}{P} \right)_{P=P} = \int_{P=0}^{P=P} \frac{Z-1}{P} dP$$

$$dG = RT d \ln f = RT d \ln \left(\frac{f}{P} \right) + RT d \ln P$$

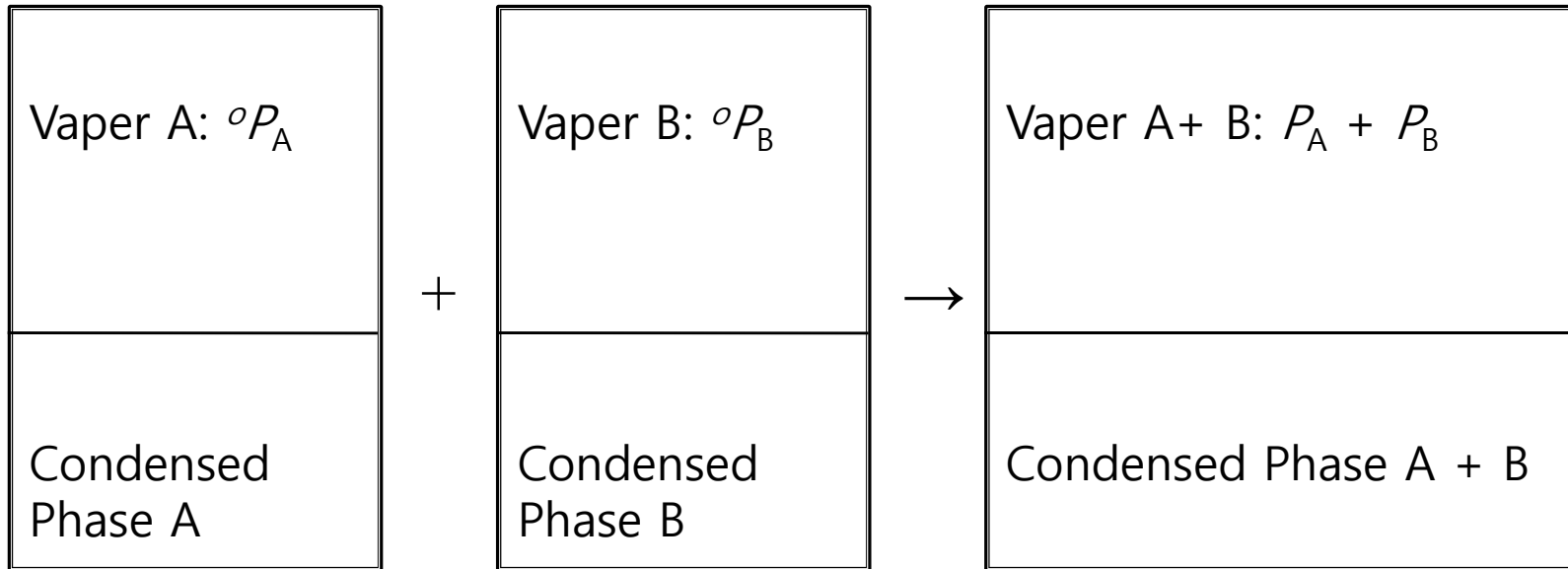


Example) Difference between the Gibbs energy at P=150 atm and P=1 atm for 1 mole of nitrogen at 0 °C

$$\Delta G = RT \ln \left(\frac{f}{P} \right)_{150} + RT \ln 150 = -76 + 11373 = 11297 \text{ J}$$



Solution Thermodynamics - Mixture of Condensed Phases



$${}^{\circ}G_A^{vapor} = {}^{\circ}G_A^{condensed}$$

$${}^{\circ}G_B^{vapor} = {}^{\circ}G_B^{condensed}$$

$$\bar{G}_A^{vapor} = \bar{G}_A^{condensed}$$

$$\bar{G}_B^{vapor} = \bar{G}_B^{condensed}$$

$$\Delta G^{mix} = \sum_i n_i \bar{G}_i - \sum_i n_i {}^{\circ}G_i \Rightarrow \sum_i n_i RT \ln \frac{p_i}{p_i^{\circ}} \quad \text{for gas}$$



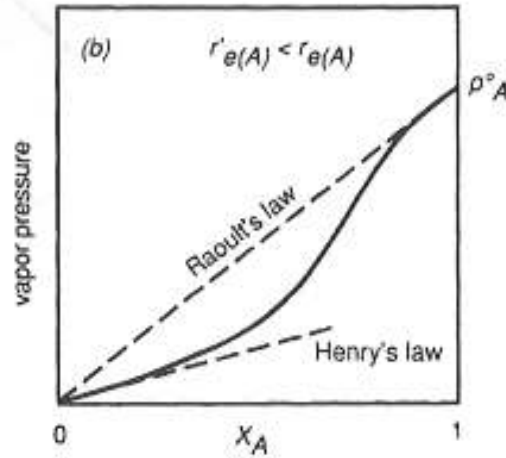
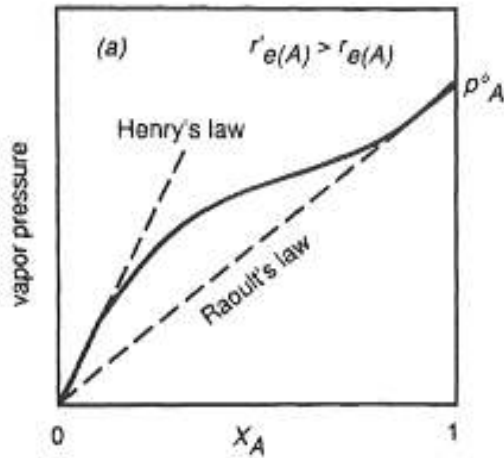
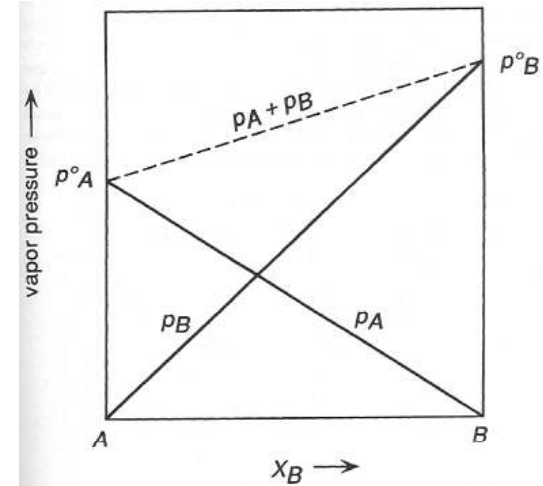
Solution Thermodynamics - ideal vs. non-ideal solution

Ideal Solution

$$r_{e(i)} = kp_i^o \quad r_{e(i)}x_i = kp_i \quad p_i = x_i p_i^o$$

Nonideal Solution

$$r'_{e(i)} x_i = kp_i \quad p_i = \frac{r'_{e(i)}}{r_{e(i)}} x_i p_i^o \quad p_i = k_i x_i p_i^o$$



Solution Thermodynamics - Thermodynamic Activity

$$G(P_2, T) - G(P_1, T) = RT \ln \frac{P_2}{P_1}$$

Thermodynamic Activity of a Component in Solution

$$a_i = \frac{f_i}{f_i^o} \quad \rightarrow \quad a_i = \frac{P_i}{P_i^o} \quad \Rightarrow \quad x_i \quad \text{for ideal solution}$$

Draw a composition-activity curve for an ideal and non-ideal solution

Henrian vs. Raoultian



Solution Thermodynamics - Partial Molar Property

$$Q' = Q'(T, P, n_1, n_2, \dots, n_c)$$

$$dQ' = \left(\frac{\partial Q'}{\partial T} \right)_{P, n_j, n_k, \dots} dT + \left(\frac{\partial Q'}{\partial P} \right)_{T, n_j, n_k, \dots} dP + \sum_{i=1}^c \left(\frac{\partial Q'}{\partial n_i} \right)_{T, P, n_j \neq n_i} dn_i$$

▷ Partial Molar Quantity $\bar{Q}_i = \left(\frac{\partial Q'}{\partial n_i} \right)_{T, P, n_j \neq n_i}$

$$dQ'_{T, P} = \sum_{k=1}^c \bar{Q}_k dn_k$$

$$Q' = \sum_{k=1}^c \bar{Q}_k n_k$$

$$\sum_{k=1}^c n_k d\bar{Q}_k = 0$$

▷ Molar Properties of Mixture

Gibbs-Duhem Equation

$$dQ = \sum_{k=1}^c \bar{Q}_k dX_k$$

$$Q = \sum_{k=1}^c X_k \bar{Q}_k$$

$$\sum_{k=1}^c x_k d\bar{Q}_k = 0$$



Solution Thermodynamics - Partial Molar Quantity of Mixing

definition of solution and mechanical mixing

$$\Delta Q'_{mix} = Q' - {}^o Q'$$

$${}^o Q' = \sum_{k=1}^c {}^o Q_k n_k$$

where ${}^o Q$ is a pure state value per mole

$$\Delta Q'_{mix} = \sum_{k=1}^c (\bar{Q}_k - {}^o Q_k) n_k = \sum_{k=1}^c \Delta \bar{Q}_k n_k$$

왜 partial molar quantity를 사용해야 하는가?



Solution Thermodynamics - Partial Molar Quantities

$$G' = n_A {}^\circ G_A + n_B {}^\circ G_B + RT(n_A \ln a_A + n_B \ln a_B)$$

$$G' = n_A \Delta {}^\circ G_A^{ref \rightarrow phase} + n_B {}^\circ G_B^{ref \rightarrow phase} + RT(n_A \ln a_A + n_B \ln a_B)$$

$$G_m = x_A {}^\circ G_A + x_B {}^\circ G_B + RT(x_A \ln a_A + x_B \ln a_B)$$

$$G_m = x_A {}^\circ G_A + x_B {}^\circ G_B + RT(x_A \ln x_A + x_B \ln x_B) + RT(x_A \ln \gamma_A + x_B \ln \gamma_B)$$

$$G_m = x_A {}^\circ G_A + x_B {}^\circ G_B + RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B L_{AB}$$



Solution Thermodynamics - Partial Molar Quantities

Evaluation of Partial Molar Properties in 1-2 Binary System

- Partial Molar Properties from Total Properties

$$\bar{Q}_2 = Q + (1 - X_2) \frac{dQ}{dX_2} \quad \text{example) } \Delta H_{mix} = aX_1X_2$$

- Partial molar & Molar Gibbs energy $\Delta \bar{G}_i^M = \bar{G}_i - {}^oG_i = RT \ln a_i$

$$G_m = x_A {}^oG_A + x_B {}^oG_B + RT(x_A \ln a_A + x_B \ln a_B)$$

Gibbs energy of mixing vs. Gibbs energy of formation

- Graphical Determination of Partial Molar Properties: **Tangential Intercepts**
- Evaluation of a PMP of one component from measured values of a PMP of the other

$$X_1 d\Delta \bar{Q}_1 + X_2 d\Delta \bar{Q}_2 = 0 \quad d\Delta \bar{Q}_1 = -\frac{X_2}{X_1} d\Delta \bar{Q}_2$$

$$\Delta \bar{Q}_1 = \int_{X_2=0}^{X_2} -\frac{X_2}{X_1} d\Delta \bar{Q}_2 = -\int_{X_2=0}^{X_2} \frac{X_2}{X_1} \frac{d\Delta \bar{Q}_2}{dX_2} dX_2 \quad \text{example) } \Delta \bar{H}_2 = aX_1^2$$



Solution Thermodynamics - Non-Ideal Solution

▷ Activity Coefficient

$$RT \ln a_k = RT \ln \gamma_k x_k$$

$$\frac{\partial(\Delta\bar{G}_i^M / T)}{\partial T} = \frac{\partial(R \ln \gamma_i)}{\partial T} = -\frac{\Delta\bar{H}_i^M}{T^2}$$

$$\frac{\partial(R \ln \gamma_i)}{\partial(1/T)} = \Delta\bar{H}_i^M$$

▷ Behavior of Dilute Solutions

$$\lim(x_k \rightarrow 1)a_k = x_k$$

$$\lim(x_k \rightarrow 0)a_k = r_k^o x_k$$



Example

1. Gibbs energy of formation과 Gibbs energy of mixing의 차이는 무엇인가?

2. Solution에서 한 성분이 Henrian 또는 Raoultian 거동을 한다는 것을 무엇을 의미하는가?

Molar Gibbs energy가 다음과 같이 표현되는 A-B 2원 Solution phase에서 각 성분은 dilute 영역에서는 Henrian 거동을, rich 영역에서는 Raoultian 거동을 보인다는 것을 증명하시오.

$$G_m = x_A {}^oG_A + x_B {}^oG_B + RT\{x_A \ln x_A + x_B \ln x_B\} + x_A x_B L$$



Solution Thermodynamics - Quasi-Chemical Model, Guggenheim, 1935.

$$E_{A-B} = W_{AA}E_{AA} + W_{BB}E_{BB} + W_{AB}E_{AB}$$

$$W_{AA} = \frac{1}{2} Nz x_A^2$$

$$W_{BB} = \frac{1}{2} Nz x_B^2$$

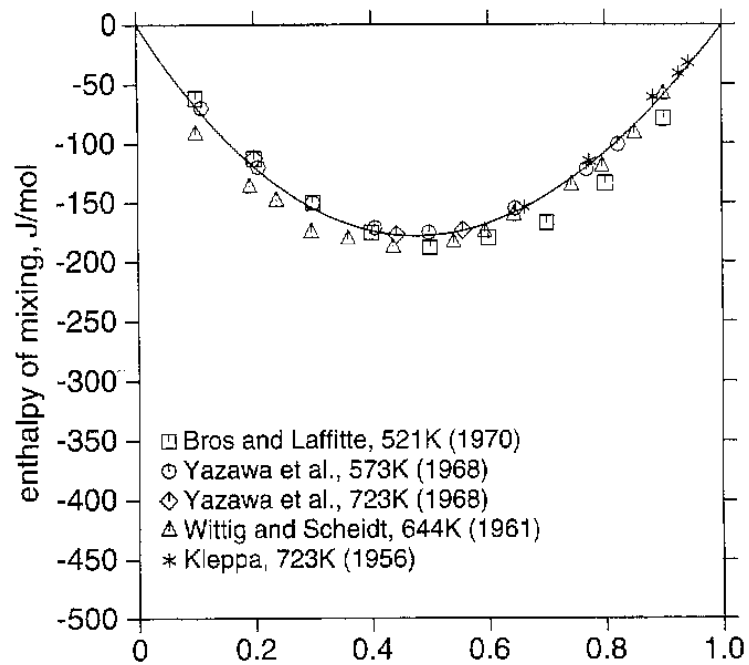
$$W_{AB} = Nz x_A x_B$$

$$E_{A-B} = \frac{Nz}{2} (x_A E_{AA} + x_B E_{BB} + x_A x_B [2E_{AB} - E_{AA} - E_{BB}])$$

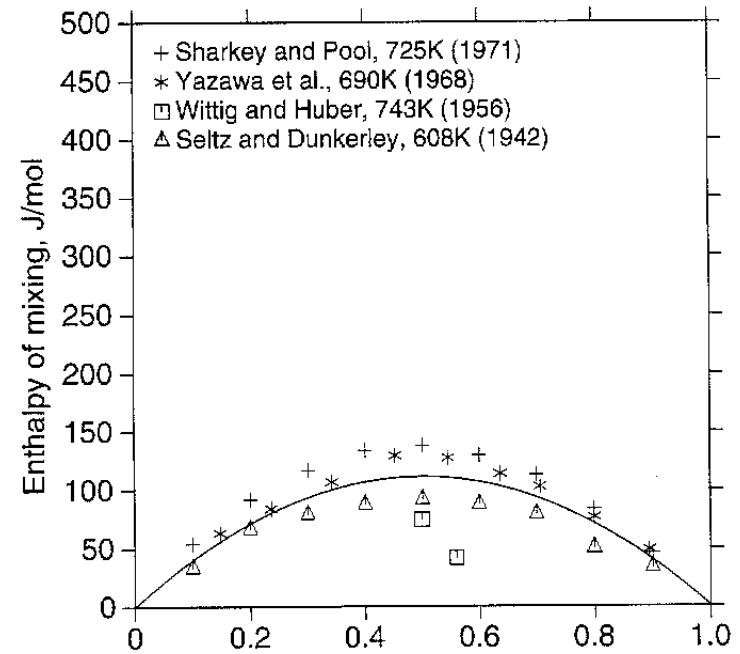


Solution Thermodynamics - Regular Solution Model

$$\Delta G_m^{xs} = x_A x_B \Omega_{AB}$$



Sn-In

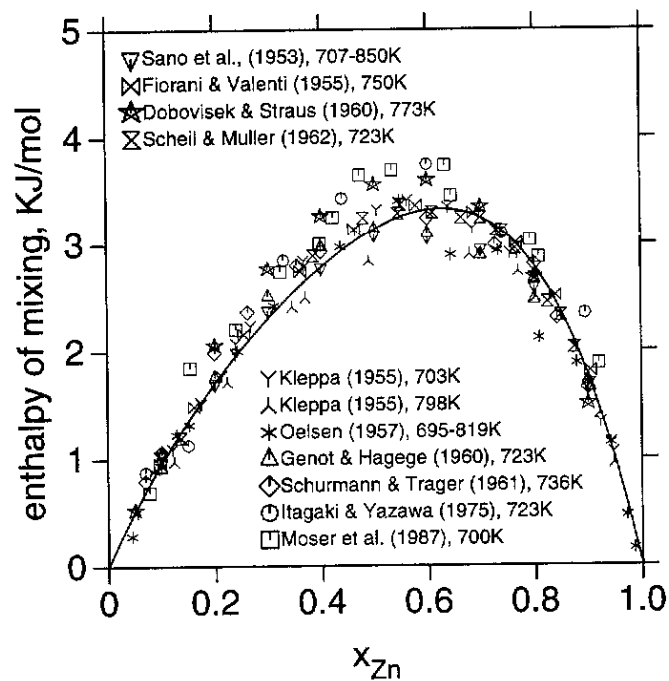


Sn-Bi

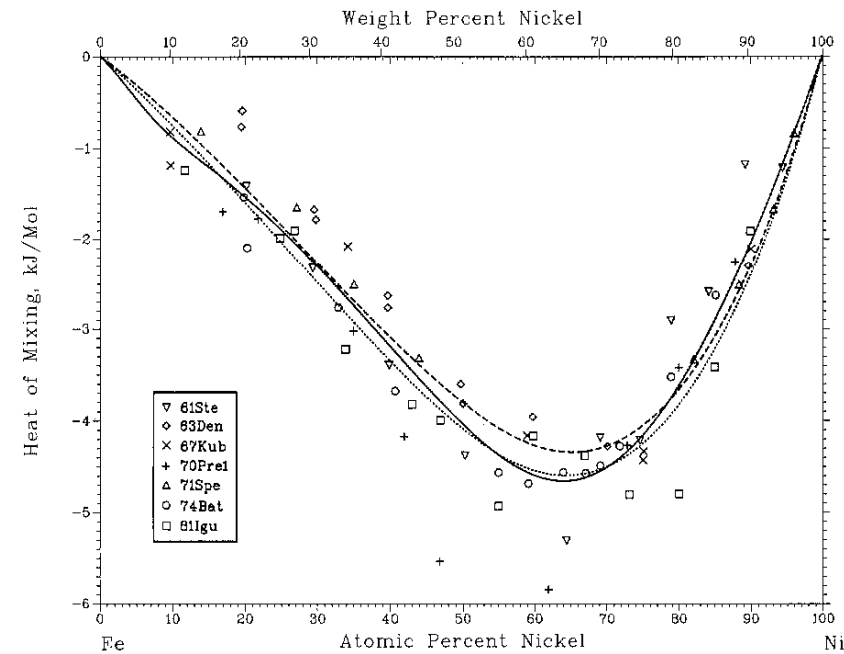


Solution Thermodynamics - Sub-Regular Solution Model

$$\Delta G_m^{xs} = x_A x_B [{}^0\Omega_{AB} + (x_B - x_A) {}^1\Omega_{AB}]$$



Sn-Zn



Fe-Ni



Solution Thermodynamics - Regular Solution Model

$$G_m = x_A {}^oG_A + x_B {}^oG_B + RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B \Omega_{AB}$$

- **Composition and temperature dependence of Ω**
- **Extension into ternary and multi-component system**
- **Sublattice Model**
- **Inherent Inconsistency**



Thermodynamics

Multi-component Heterogeneous System

Byeong-Joo Lee

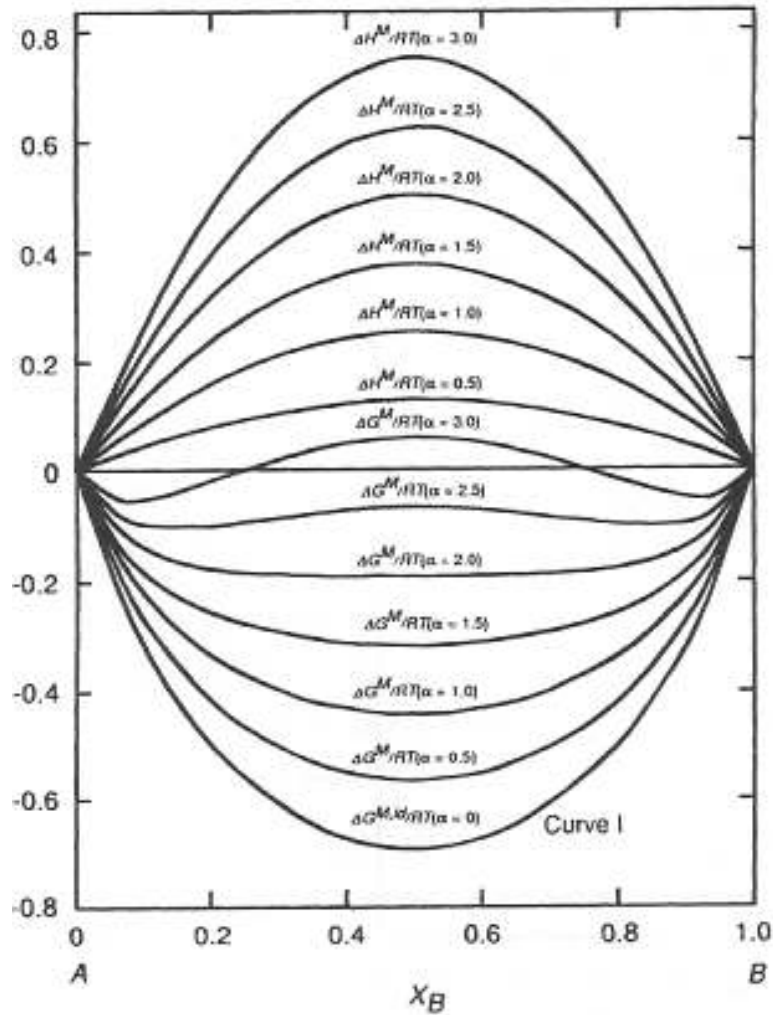
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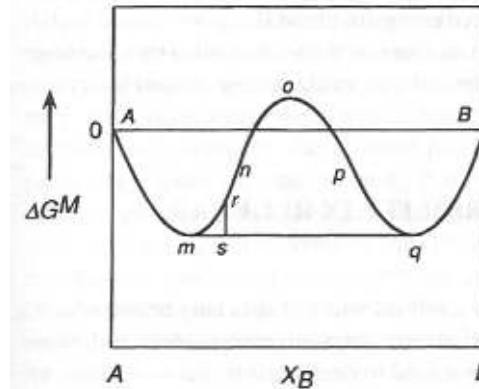
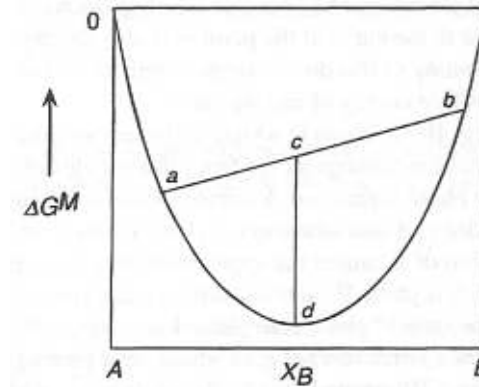
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Property of a Regular Solution



$$\Delta G^{xs} = \Delta H^{mix} = \Omega \cdot x_A x_B$$



Property of a Regular Solution

$$\Delta G^M = RT(X_A \ln X_A + X_B \ln X_B) + RT\alpha X_A X_B$$

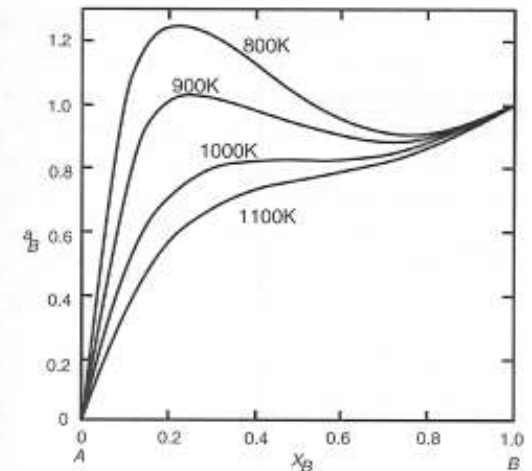
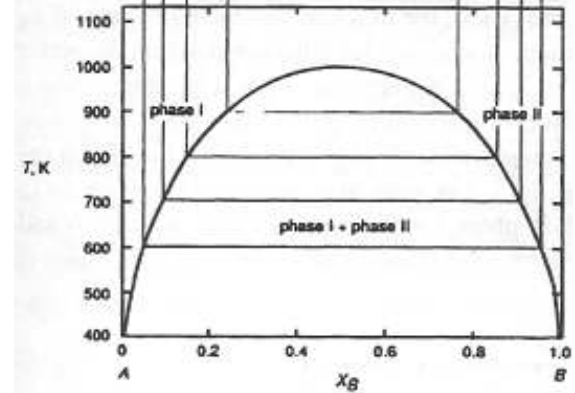
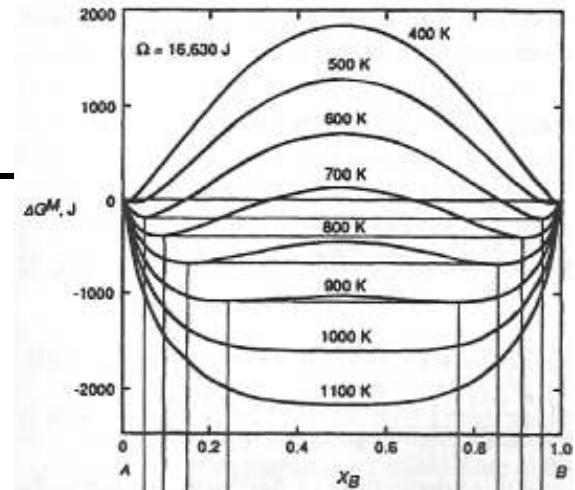
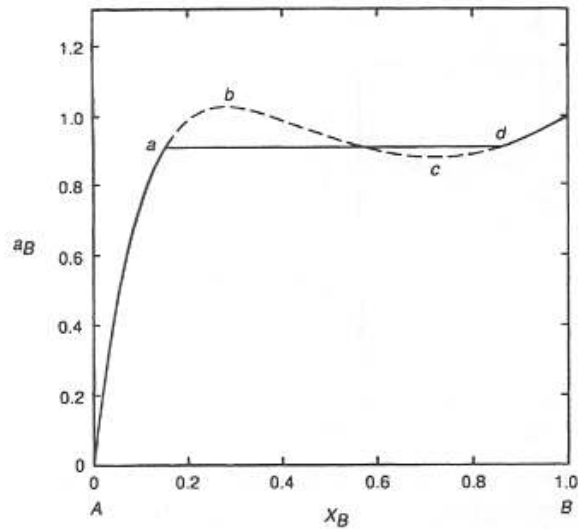
$$\frac{\partial \Delta G^M}{\partial X_B} = RT \left[\ln \frac{X_B}{X_A} + \alpha(X_A - X_B) \right]$$

$$\frac{\partial^2 \Delta G^M}{\partial X_B^2} = RT \left(\frac{1}{X_A} + \frac{1}{X_B} - 2\alpha \right)$$

$$\frac{\partial^3 \Delta G^M}{\partial X_B^3} = RT \left(\frac{1}{X_A^2} - \frac{1}{X_B^2} \right)$$

$$\Omega = RT\alpha$$

$$T_{cr} = \frac{\Omega}{2R}$$

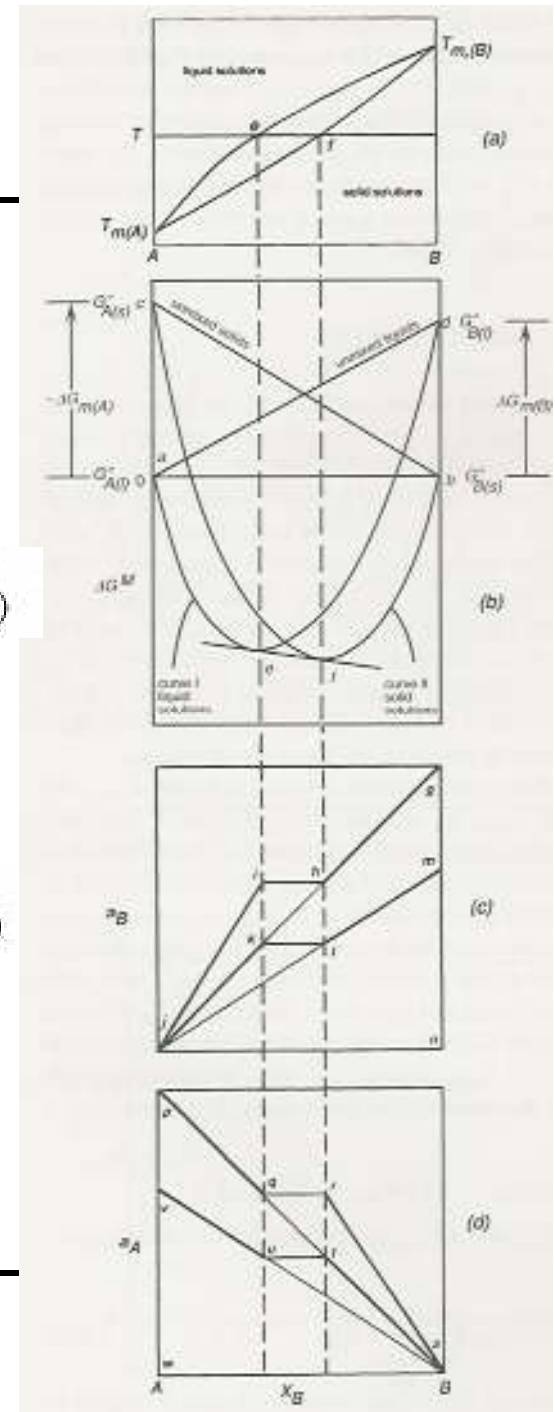


Standard States

$$\Delta G = \Delta G^{M,id} = RT(X_A \ln X_A + X_B \ln X_B)$$

$$\Delta G_{(l)}^M = RT(X_A \ln X_A + X_B \ln X_B) + X_B \Delta G_{m(B)}^\circ$$

$$\Delta G_{(s)}^M = RT(X_A \ln X_A + X_B \ln X_B) - X_A \Delta G_{m(A)}^\circ$$



Standard States

If pure solid B is chosen as the standard state and is located at the point g in Fig. 10.8c, then the length gn is, by definition, unity, and this defines the solid standard state activity scale. The line $ghij$ then represents a_B in the solutions with respect to solid B having unit activity at g . The line is obtained from the variation of the tangential intercepts from the curve $aefb$ to the $X_B = 1$ axis, measured from the point b . On this activity scale Raoult's law is given by kg , and the points i and h represent, respectively, the activity of B in the coexisting liquid solution e and solid solution f . The point m represents the activity of pure liquid B measured on the solid standard state activity scale of B . This activity is less than unity, being given by the ratio mn/gn . For B in any state along the $aefb$ Gibbs free energy curve, in which state the partial molar Gibbs free energy of B is \bar{G}_B , the following relations hold:

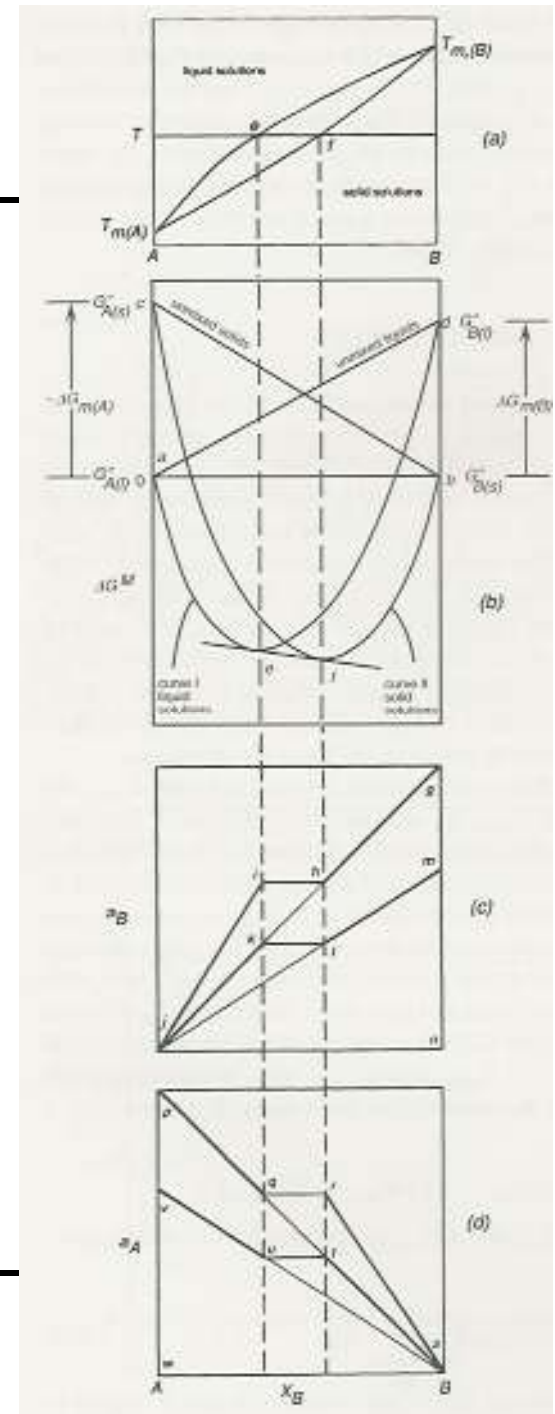
$$\bar{G}_B = G_{B(l)}^\circ + RT \ln (a_B \text{ with respect to liquid } B)$$

and

$$\bar{G}_B = G_{B(s)}^\circ + RT \ln (a_B \text{ with respect to solid } B)$$

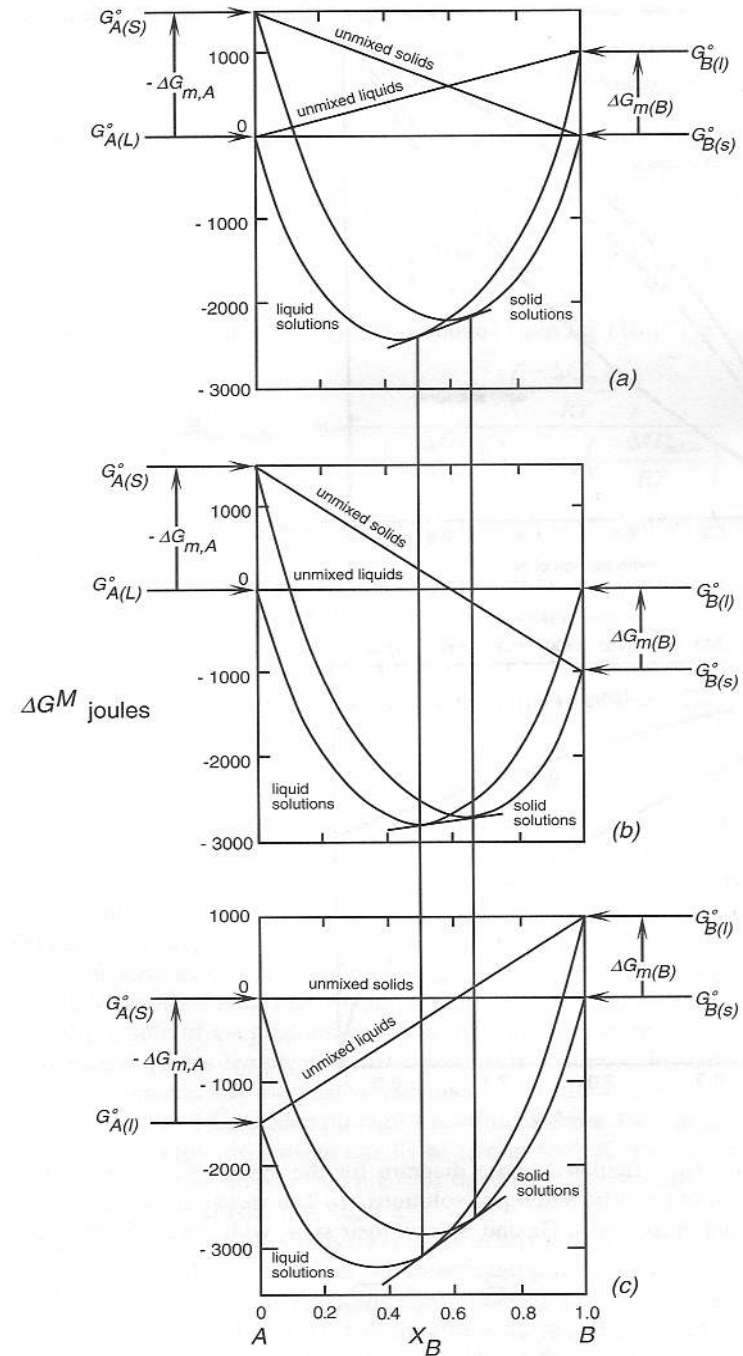
Thus

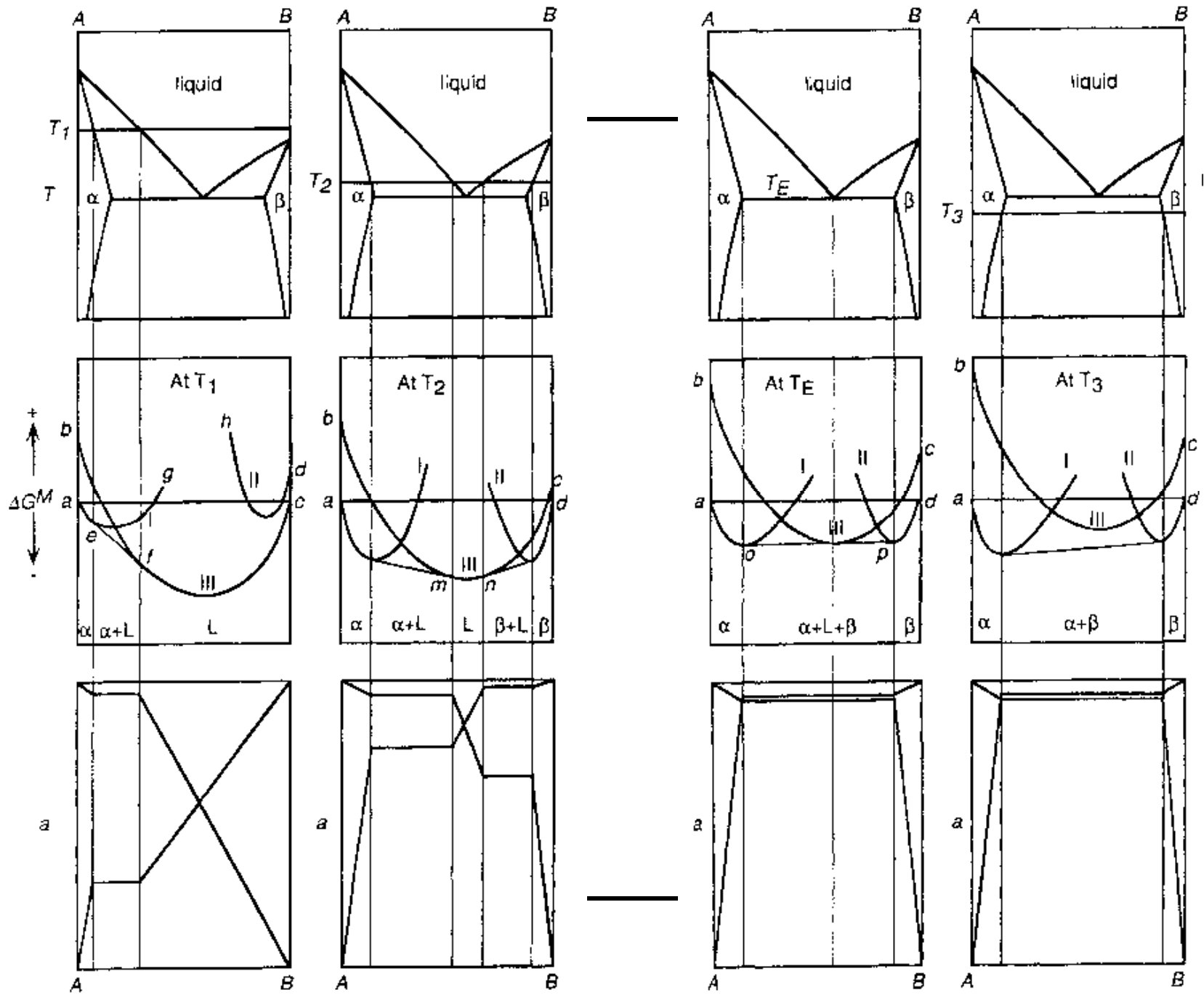
$$G_{B(l)}^\circ - G_{B(s)}^\circ = \Delta G_{m(B)}^\circ = RT \ln \left(\frac{a_B \text{ with respect to solid } B}{a_B \text{ with respect to liquid } B} \right) \quad (10.21)$$



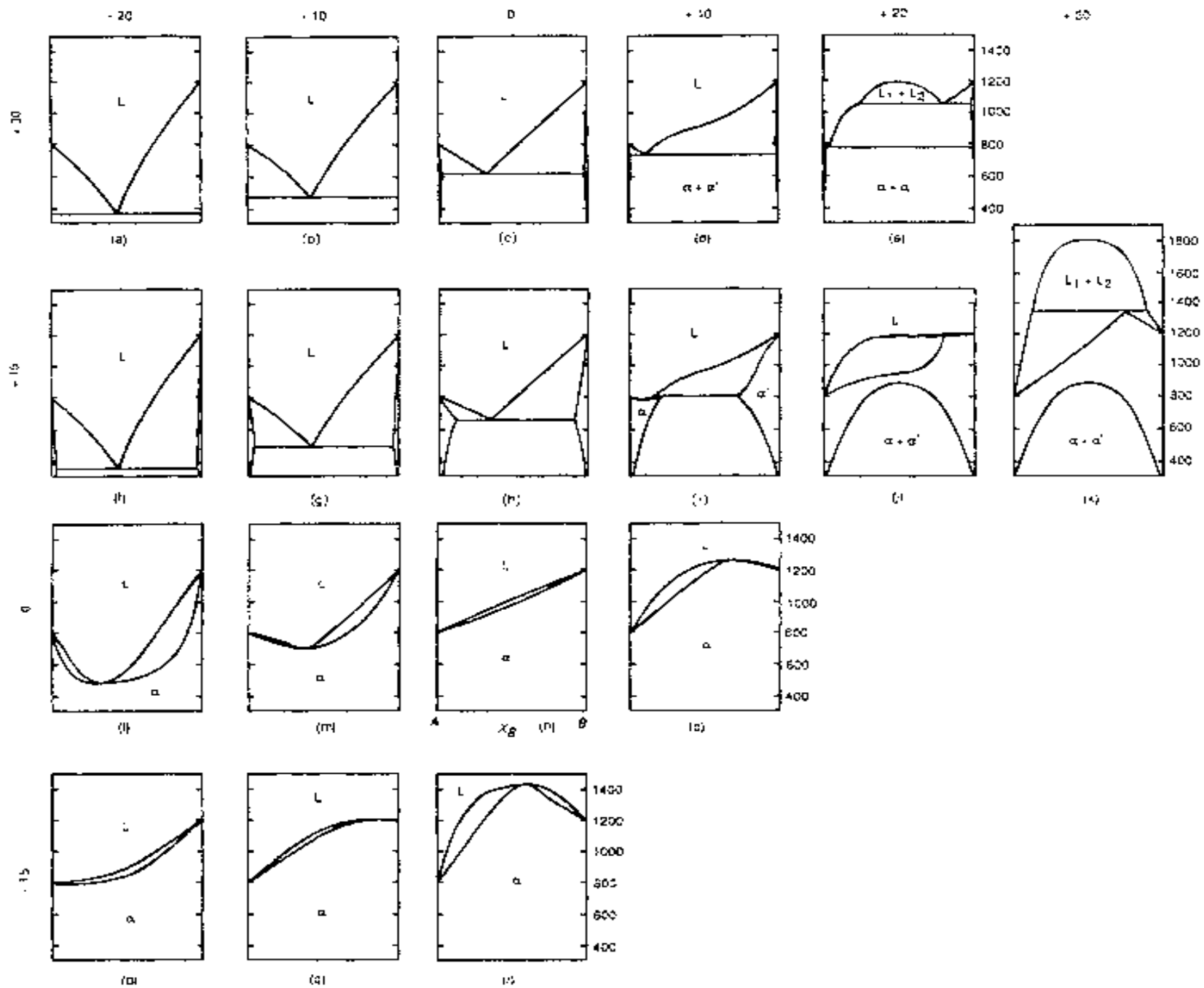
Standard States

Which standard states shall we use?

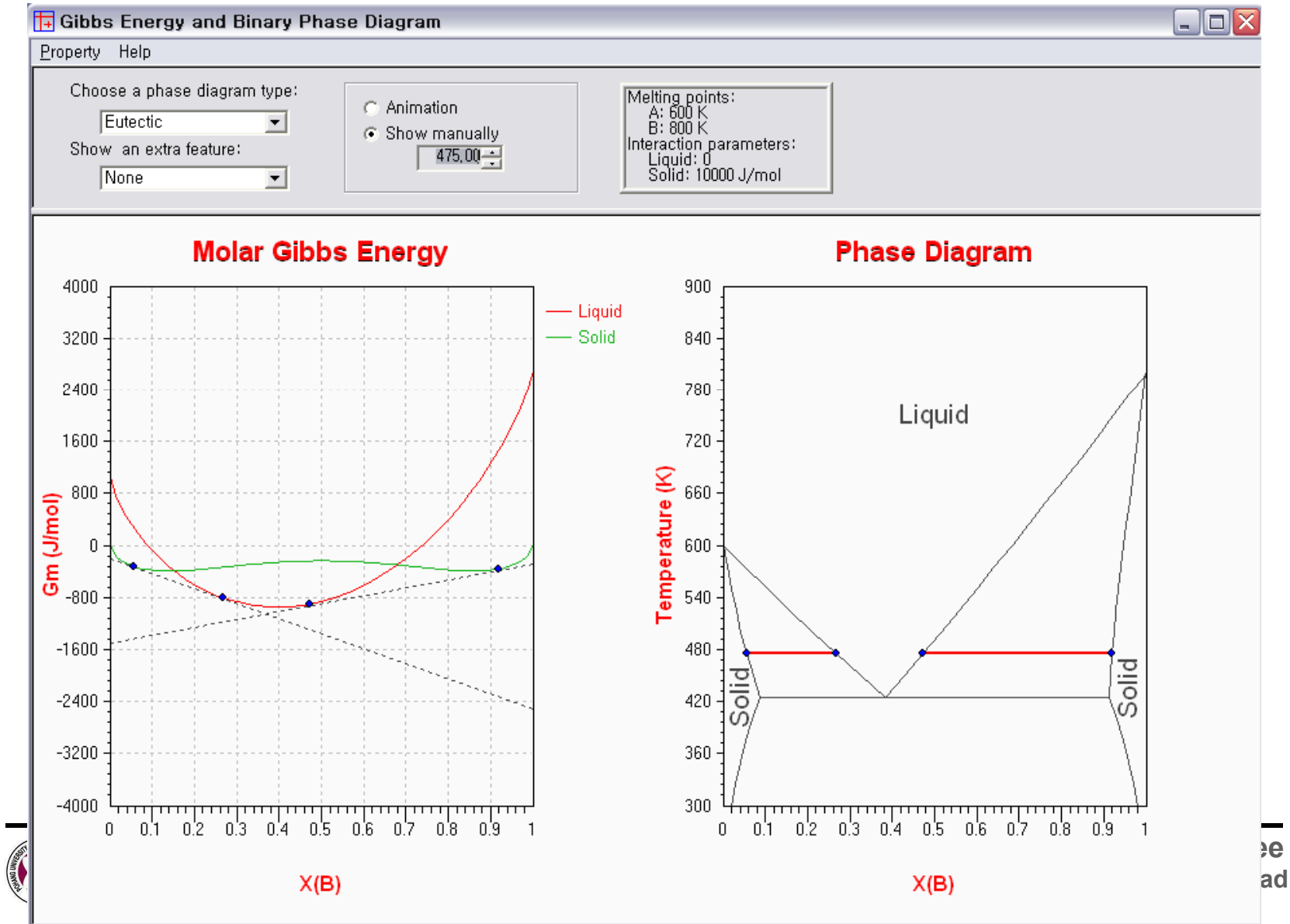




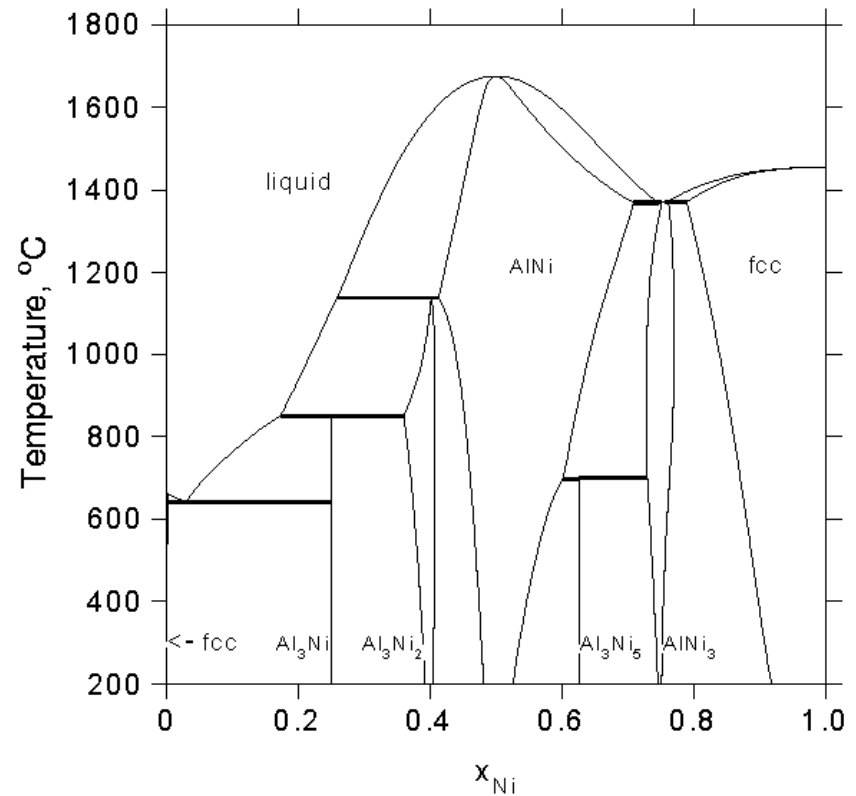
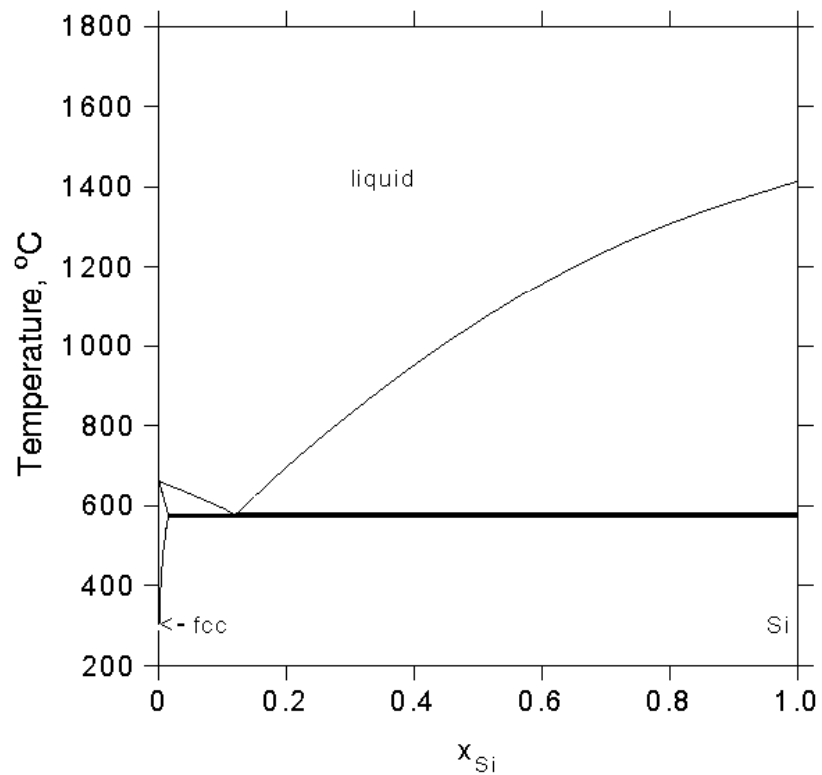
Ω_1 , kilojoules



Phase Diagrams - Relation with Gibbs Energy of Solution Phases



Phase Diagrams - Binary Systems



Phase Equilibrium

1. Conditions for equilibrium

$$dS'_{sys,iso} = \left(\frac{1}{T^\alpha} - \frac{1}{T^\beta} \right) dU'^\alpha + \left(\frac{P^\alpha}{T^\alpha} - \frac{P^\beta}{T^\beta} \right) dV'^\alpha - \sum_k \left(\frac{\mu_k^\alpha}{T^\alpha} - \frac{\mu_k^\beta}{T^\beta} \right) dn_k^\alpha$$

2. Gibbs Phase Rule

$$f = p(c + 1) - (p - 1)(c + 2) = c - p + 2$$

3. How to interpret Binary and Ternary Phase Diagrams

▷ Lever-Rule

$$n_T x^o = n^\varepsilon x^\varepsilon + n^L x^L$$

$$x^o = f^\varepsilon x^\varepsilon + f^L x^L = f^\varepsilon x^\varepsilon + (1 - f^\varepsilon) x^L = f^\varepsilon (x^\varepsilon - x^L) + x^L$$

$$f^\varepsilon = \frac{x^L - x^o}{x^L - x^\varepsilon}$$

$$f^L = \frac{x^o - x^\varepsilon}{x^L - x^\varepsilon}$$



Driving force of CVD Deposition - from N.M. Hwang, SNU

※ Example: Deposition of Silicon

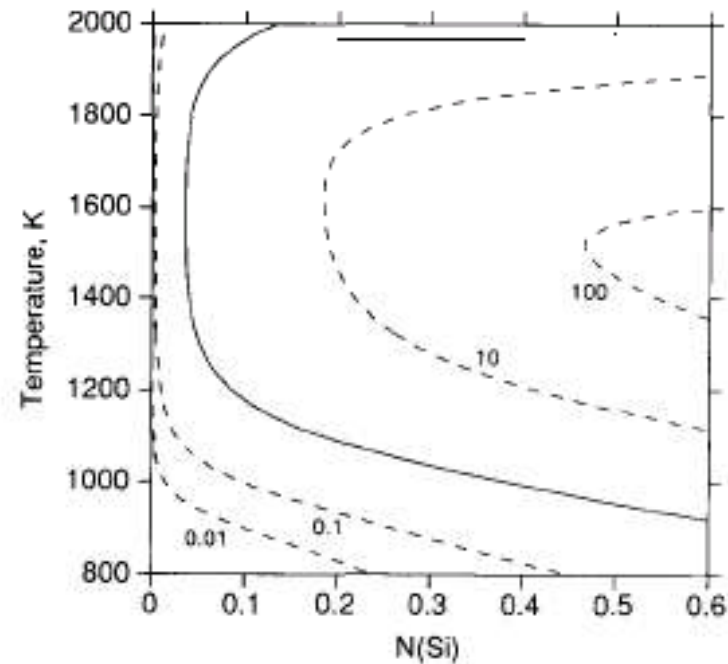
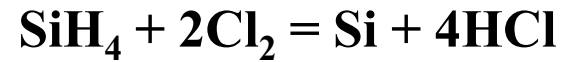


Fig. 1. CVD phase diagram of the Si-Cl-H system at 10666 Pa and composition of $N(\text{H}) = 200$ and $N(\text{Cl}) = 1$. The dashed

