CH6 C_p, Enthalpy & Entropy as a function of T, $C_p(T)$, H(T), $\triangle$H(T), S(T), $\triangle$S(T), 3rd Law of Thermodynamics

§ Heat Capacity

$$C_v \equiv \left(\frac{\delta Qrev}{dT}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v = T\left(\frac{\partial S}{\partial T}\right)_v$$

$$C_p \equiv \left(\frac{\delta Qrev}{dT}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

∴ $dU_v = C_v dT$, $dU_v' = nC_v dT$ (n moles)
$dH_p = C_p dT$, $dH_p' = nC_p dT$

constant P, $\Delta H_p = H_2(T_2, P) - H_1(T_1, P) = \int_{T1}^{T2} C_p dT \cdots (*1)$

$$dS_p = \frac{C_p}{T} dT \quad \therefore \Delta S_p = S_2(T_2, P) - S_1(T_1, P) = \int_{T1}^{T2} \frac{C_p}{T} dT \cdots (*2)$$

In order to do integration, $C_p(T)$ must be known
Experimental experience: for the same material state
$C_p = a + bT + CT^{-2}$ (p546 Table A2)

e.g. 298K $\leqq$ T $\leqq$ 1478K, α-ZrO_2

$C_p = 69.62 + (7.53 \times 10^{-3})T - (14.06 \times 10^{-5})T^{-2}$ (J/mole · K)

1478K $\leqq$ T $\leqq$ Tm=2950K, β-ZrO2

$C_p = 74.48$ (J/mole · K)

* Kopp's Rule: $C_p(A_m B_n) = mC_p(A) + nC_p(B)$
Heat capacity of a solid compound is equal to sum of C_p of its constituent elements.

§ $H_p(T)$, $\triangle$H(T), and Q_p (Heat of Reaction)

* constant P=1 atm
closed system of fixed composition ; $T_1 \rightarrow T_2$

$$\Delta H_p = H_2(T_2, P) - H_1(T_1, P) = \int_{T1}^{T2} C_p dT$$

$$\because dH_p \equiv TdS \equiv \delta Q_p$$

$$\therefore \triangle H_p = Q_p$$

* H does not have an absolute value
<u>convention</u>: "Elements" in their stable state at 298 K (25 ℃), 1 atm (STP),
$H \equiv 0$

$$\therefore H(T) = \int_{298}^{T} C_p dT$$
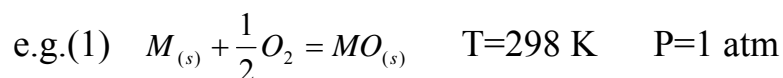
* Chemical Reaction:

A+B=AB   at (T_0, P_0)

$\triangle H(T_0, P_0) = H_{AB}(T_0, P_0) - [H_A(T_0, P_0) + H_B(T_0, P_0)]$ <Hess's Law>
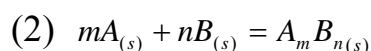
$\triangle H > 0$, endothermic

$\triangle H < 0$, exothermic

* Enthalpy of a compound at 298 K is simply heat of formation of the compound from its elements at 298 K.

e.g.(1) $M_{(s)} + \frac{1}{2}O_2 = MO_{(s)}$ T=298 K   P=1 atm

$$\Delta H_{298} = H_{MO} - H_M - \frac{1}{2}H_{O_2}$$

$\because H_M \equiv 0$, $H_{O_2} \equiv 0$ at 298 K

$\therefore H_{MO} = \triangle H_{298}$ (Data, P547 TableA-3)

(2) $mA_{(s)} + nB_{(s)} = A_m B_{n(s)}$

$$H_{A_m B_n} = \Delta H_{298}$$ (Data. 查表)

* Equilibrium phase transition:

equil. melting $A_{(s)} \rightarrow A_{(l)}$ T=T_{mA}=T_1
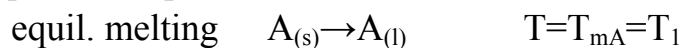
$\triangle H_m = H_{A(l)} - H_{A(s)}$ heat of melting (fusion)

* Non-equilibrium phase transition:

$A_{(s)} \rightarrow A_{(l)}$ T=$T_2 \neq T_{mA}$

$\triangle H_T(T_2)=?$

$\therefore \triangle H_{T2}=H_{A(l)}(T_2)-H_{A(s)}(T_2)$

i.e. $\triangle H(d \to c)=H_c-H_d=\triangle H(d \to a)+\triangle H(a \to b)+\triangle H(b \to c)$

$$\therefore \Delta H_{T_2} = \int_{T2}^{T1} C_{p(s)} dT + \left[H_{A(l)}(T_1) - H_{A(s)}(T_1) \right] + \int_{T1}^{T2} C_{p(l)} dT$$

$$= \Delta H_m + \int_{T1}^{T2} C_{p(l)} dT - \int_{T1}^{T2} C_{p(s)} dT$$

$$= \Delta H_m + \int_{T1}^{T2} [C_{p(l)} - C_{p(s)}] dT$$

$$\therefore \Delta H_m(T) = \Delta H_m + \int_{T_m}^{T} \Delta C_p dT$$

If $\triangle H_m$, Tm are known, them heat of melting at any other temperature can be calculated. When $C_{p(s)}$ and $C_{p(l)}$ are known.

Note: $\triangle H_m > 0$ (endothermic)

* In general (phase transition or reaction)
    state 1 → state 2

$$C_{p(1)} = \left(\frac{\partial H_1}{\partial T} \right)_p$$

$$C_{p(2)} = \left(\frac{\partial H_2}{\partial T} \right)_p$$

$$\therefore \left(\frac{\partial H_2}{\partial T} \right)_p - \left(\frac{\partial H_1}{\partial T} \right)_p = C_{p(2)} - C_{p(1)}$$

$$\left[\frac{\partial (H_2 - H_1)}{\partial T} \right]_p = \Delta C_p$$

or $\left[\frac{\partial \Delta H}{\partial T} \right]_p = \Delta C_p$

$$\Delta H = \Delta H_{T_2} - \Delta H_{T_1} = \int_{T1}^{T2} \Delta C_p dT$$

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T1}^{T2} \Delta C_p dT$$

If $\triangle H > 0$ (endothermic)

e.g. (1) $S \to l$, $\triangle H_m > 0$

(2) state 1 $\to$ state 2
low T phase $\to$ high T phase
Heating $\implies$ system moves to high-temp phase

"Le Chatelier's Principle":
When a system, which is at equilibrium, is subjected to an external influence, the system moves in the direction which nullifies the effect of external influence.

* If heat of formation of an oxide is known, then heat of oxidation reaction at other temperature can be calculated.

$$Pb + \frac{1}{2}O_2 = PbO \qquad \triangle H(T) = ?$$
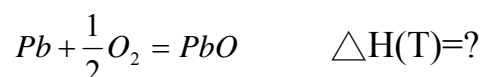
Given Table 6.1
$\begin{cases} \triangle H_{PbO(298)} = H_{PbO(298)} = -219000 \text{ J/K} \cdot \text{mole} \\[2mm] C_p, Pb_{(s)} = 23.6 + 9.75 \times 10^{-3}T \text{ J/K} \cdot \text{mole } 298K \leqq T \leqq T_{m,Pb} \\[2mm] C_p, Pb_{(l)} = 32.4 + 31 \times 10^{-3}T \text{ J/K} \cdot \text{mole} \quad T_{m,Pb} \leqq T \leqq 1200K \\[2mm] C_p, PbO_{(s)} = 37.9 + 26.8 \times 10^{-3}T \text{ J/K} \cdot \text{mole } 298K \leqq T \leqq T_{m,PbO} \\[2mm] C_p, O_{2(g)} = 29.96 + 4.18 \times 10^{-3}T - 1.67 \times 10^{5}T^{-2}, 298 \leqq T \leqq 3000 \\[2mm] \triangle H_{m,Pb} = 4810 \text{ J/ mole} \\[2mm] T_{m,Pb} = 680 \text{ K}, \qquad T_{m,PbO} = 1159 \text{ K} \end{cases}$

$\therefore$ $\begin{cases} H_{Pb}(T) = 0 + \int_{298}^{T_m} C_p, Pb_{(s)}dT + \Delta H_m, Pb + \int_{T_m}^{T} C_p, Pb_{(l)}dT \\[3mm] H_{\frac{1}{2}O_2}(T) = 0 + \int_{298}^{T} C_p, O_2(g)dT \qquad T < 1000K \\[3mm] H_{PbO}(T) = -219000 + \int_{298}^{T} C_p, PbO_{(s)}dT \end{cases}$

(1) For 298 K $\leqq T \leqq T_{m,}$Pb(600K), $\triangle H_{PbO}(T) = ?$

$\therefore \triangle H_{PbO}(T) = H_{PbO}(T) - [H_{Pb}(T) + H_{1/2O2}(T)]$

i.e. $\Delta H(f \to g) = \Delta H(f \to a) + \Delta H(a \to d) + \Delta H(d \to g)$

$$= \int_T^{298} [C_p, Pb_{(s)} + \frac{1}{2} C_p, O_{2(g)}] dT + \Delta H_{PbO}(298) + \int_{298}^T C_p, PbO_{(s)} dT$$

$$= \Delta H_{PbO}(298) + \int_{298}^T C_p, PbO_{(s)} dT - \int_{298}^T [C_p, Pb_{(s)} + \frac{1}{2} C_p, O_{2(g)}] dT$$

$$= \Delta H_{PbO}(298) + \int_{298}^T \{C_p, PbO_{(s)} - [C_p, Pb_{(s)} + \frac{1}{2} C_p, O_{2(g)}]\} dT$$

$$\therefore \Delta H_{PbO}(T) = \Delta H_{PbO}(298) = \int_{298}^T \Delta C_p \cdot dT$$

$$\Delta C_p = C_p, PbO_{(s)} - C_p, Pb_{(s)} - \frac{1}{2} C_p, O_{2(g)}$$

(2) For $T_m, Pb(600K) \leqq T \leqq T_m, Pb(1159K)$, $\triangle H_{PbO}(T) = ?$

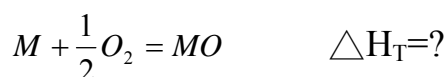$$\Delta H(l \to e) = \Delta H(l \to k) + \Delta H(k \to j) + \Delta H(j \to a) + \Delta H(a \to d) + \Delta H(d \to e)$$

$$= \int_T^{600} [C_p, Pb_{(l)} + \frac{1}{2} C_p, O_{2(g)}] dT + (-\Delta H_m) + \int_{660}^{298} [C_p, Pb_{(s)} + \frac{1}{2} C_p, O_{2(g)}] dT$$

$$+ \Delta H_{PbO}(298) + \int_{298}^T C_p, PbO_{(s)} dT + \int_{600}^T C_p, PbO_{(s)} dT$$

$$\Delta H_{PbO}(T) = \Delta H_{PbO}(298) - \Delta H_m + \int_{298}^{680} \Delta C_{p(s)} dT + \int_{600}^T \Delta C_{p(l)} dT$$

$$\Delta C_{p(s)} = C_p, PbO_{(s)} - C_p, Pb_{(s)} - \frac{1}{2} C_p, O_{2(g)}$$

$$\Delta C_{p(l)} = C_p, PbO_{(l)} - C_p, Pb_{(l)} - \frac{1}{2} C_p, O_{2(g)}$$

* General oxidation

$$M + \frac{1}{2} O_2 = MO \qquad \triangle H_T = ?$$

If: $T_{m,M} < T_{m,MO} < T$

$$\therefore \Delta H_T = \Delta H_{298} + \int_{298}^{T_{m,M}} [C_{p,MO(s)} - C_{p,M(s)} - \frac{1}{2} C_{p,O2(g)}] dT$$

$$- \Delta H_{m,M} + \int_{T_{m,M}}^{T_{m,MO}} [C_{p,MO(s)} - C_{p,M(l)} - \frac{1}{2} C_{p,O2(g)}] dT$$

$$+ \Delta H_{m,MO} + \int_{T_{m,MO}}^T [C_{p,MO(l)} - C_{p,M(l)} - \frac{1}{2} C_{p,O2(g)}] dT$$

§ S(T) and the 3rd law of thermodynamics

2nd law: $dS \equiv \dfrac{\delta Q_{rev}}{T}$

constant P: $dS = \dfrac{\delta Q_p}{T} = \dfrac{dH_p}{T} = \dfrac{C_p dT}{T}$

* For a closed system of fixed composition, $T_1 \rightarrow T_2$

$\Delta S = S(T_2, p) - S(T_1, p) = \displaystyle\int_{T_1}^{T_2} \dfrac{C_p}{T} dT$

$\therefore S(T) = S_0 + \displaystyle\int_0^T \dfrac{C_p}{T} dT$

S_0: molar entropy at 0°k

* S_0=?

<u>Nernst (1906) postulation:</u>

For chemical reactions between pure solids or pure liquids

When T→0 $\left(\dfrac{\partial \Delta G}{\partial T}\right)_p \rightarrow 0$ ($\triangle$S→0)

$\left(\dfrac{\partial \Delta H}{\partial T}\right)_p \rightarrow 0$ ($\triangle$C$_p$→0)

∵G=H－TS

dG=dH－TdS－SdT

constant T,P   dG=dH－TdS

$\therefore \triangle$G=$\triangle$H－T$\triangle$S

$\left(\dfrac{\partial \Delta G}{\partial T}\right)_p = \left(\dfrac{\partial \Delta H}{\partial T}\right)_p - T\left(\dfrac{\partial \Delta S}{\partial T}\right)_p - \Delta S$

∵dG=－SdT+VdP

$\therefore \left(\dfrac{\partial G}{\partial T}\right)_p = -S$ $\left(\dfrac{\partial \Delta G}{\partial T}\right)_p = -\Delta S$

Note: $\left(\dfrac{\partial G_2}{\partial T}\right)_p - \left(\dfrac{\partial G_1}{\partial T}\right)_p = -S_2 - (-S_1) = -(S_2 - S_1) = -\Delta S$

$$\therefore \left[\frac{\partial(G_2 - G_1)}{\partial T}\right]_p = \left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S$$

$$\therefore \left(\frac{\partial \Delta H}{\partial T}\right)_p - T\left(\frac{\partial \Delta S}{\partial T}\right)_p = 0$$

$$\left(\frac{\partial \Delta H}{\partial T}\right)_p = T\left(\frac{\partial \Delta S}{\partial T}\right)_p = \Delta C_p$$

Two, From Nernst postulation:

T→0   △S→0

△C_p→0   (if $\left(\frac{\partial \Delta S}{\partial T}\right)_p \not\longrightarrow \infty$)

<u>Nernst's theorem:</u>

For all reactors involving condensed substances

△S=0, at T=0

Reaction: A+B=AB

△S=S_{AB} — S_A — S_B=0,   T=0°K

If S_A=0, S_B=0 then S_{AB}=0

Therefore, S_0=0

<u>3rd Law (Plauds):</u>

Entropy of any <u>homogeneous</u> substance in <u>complete internal equilibrium</u> is zero at 0°K.

Example of non-equilibrium and inhomogeneous:

1. Glassy state: noncrystalline solid (supercooled liquid metastable state.)(kinetically not able to transform into equil.)

   glass→crystalline solid   T<T_m

   ∴ S_0(glass)≠0

2. Inhomogeneous solution:
   Nonequil. degree of order, S_0≠0   (A+%B)
3. Inhomogeneous mixing of isotopes. (pure solid)
4. Non-equilibrium concentrations of vacancy
5. Non-random orientations of molecular solids
   e.g. CO solid

§ Experimental verification of 3rd Law

* Phase transition at 0°K   α $\underline{\quad sulfur \quad}$ β   △S$_0$→0

$$\Delta S_0 = \Delta S_I + \Delta S_{II} + \Delta S_{III}$$

$$= \int_0^{T_t} \frac{C_{p(\alpha)}}{T} dT + \frac{\Delta H_t}{T_t} + \int_{T_t}^0 \frac{C_{p(l)}}{T} dT$$

$$= \frac{\Delta H_t}{T_t} + \int_{T_t}^0 \frac{[C_{p(\beta)} - C_{p(\alpha)}]}{T} dT$$

sulfur   monoclinic $T > 368.5K$ $\therefore T_t = 368.5K$

       orthorhombic $T < 368.5K$ △H$_t$=400 J/mole

Exp: $\Delta S_I = \int_0^{368.5} \frac{C_p(orth)}{T} dT = 36.86$ J/K · mole

$$\Delta S_{II} = \frac{\Delta H_t}{T_t} = \frac{400}{368.5} = 1.09 \quad \text{J/K · mole}$$

$$\Delta S_{III} = \int_{368.5}^0 \frac{C_p(mono)}{T} dT = -37.8 \quad \text{J/K · mole}$$

$$\therefore \Delta S_I + \Delta S_{II} + \Delta S_{III} = 0.15 \quad \text{J/K · mole} \approx 0 \text{ !! within exp. Error}$$

* Assign S$_0$=0

$$\therefore \boxed{S(T) = \int_0^T \frac{C_p}{T} dT}$$

(1) $S_{298} = \int_0^T \frac{C_p}{T} dT$ (see table A-3 p585)

(2) T≠298 $S(T) = S_{298} + \int_{298}^T \frac{C_p}{T} dT$

(3) 298 < T$_t$ < T ,e.g. 298 < T$_m$ < T

$$S(T) = S_{298} + \int_{298}^{T_m} \frac{C_{p,(s)}}{T} dT + \Delta S_m + \int_{T_m}^T \frac{C_{p(l)}}{T} dT$$

$$\Delta S_m = \frac{\Delta H_m}{T_m} \quad (\Delta G_m = 0)$$

* Richard's Rule:

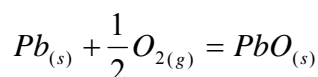   "Metals" $\Delta S_m = \frac{\Delta H_m}{T_m} \cong 8.4$ J/K · mole

exp. $\begin{cases} \text{FCC metals: } \triangle H_m = 9.61 T_m \pm 0.01 \\ \text{BCC metals: } \triangle H_m = 8.25 T_m \pm 0.19 \end{cases}$

* Trouton's Rule

"Metals" $\Delta S_b = \dfrac{\Delta H_b}{T_b} \cong 88$ J/K · mole

exp. $\begin{cases} \text{All metals} \quad \triangle H_b = 127 T_b - 43 \\ \\ T_b < 2100K \quad \triangle H_b = 87 T_b - 0.4 \end{cases}$

* Entropy change of oxidation reaction

$$Pb_{(s)} + \frac{1}{2} O_{2(g)} = PbO_{(s)}$$

$$\Delta S(T) = S_{T,PbO} - S_{T,Pb} - \frac{1}{2} S_{T,O_2}$$

$$\Delta S_{298} = S_{298,PbO} - S_{298,Pb} - \frac{1}{2} S_{298,O_2}$$

$$= 67.4 - 64.9 - \frac{1}{2} \times 205$$

$$= -100 \text{ J/K · mole}$$

$$\therefore \Delta S(T) \cong -\frac{1}{2} S_{T,O_2}$$

For Oxidation reaction of a metal, the entropy change is similar to that comsed by the dissappearance of $O_{2(g)}$

$$\because S_{(gas)} > > S_{(condensed\ phase)}$$

§ Influence of P on △H and △S

1. $H_T(P)$ dH=TdS+VdP

   dH=CpdT+V(1－αT)dP

$$\therefore \left(\frac{\partial H}{\partial P} \right)_T = T \left(\frac{\partial S}{\partial P} \right)_T + V$$

$$= -T \left(\frac{\partial V}{\partial T} \right)_p + V$$

$$= -V\alpha T + V = V(1 - \alpha T)$$

$$\therefore \text{constant T,} \quad dH_T = V(1 - \alpha T)dP$$

$$\Delta H = H(P_2, T) - H(P_1, T) = \int_{P_1}^{P_2} V(1 - \alpha T)dP$$

* Condensed phase: $\triangle H \approx V(1 - \alpha T)(P_2 - P_1)$

usually, H, S, G, C_p, α of condensed phases are insensitive to P

e.g. Fe(α) $\quad$ V=7.1 cm^3/mole

$$\begin{cases} \alpha = 3 \times 10^{-5} \text{ /K} \\ T_1 = 298K, \quad P_1 = 1 \text{ atm}, P_2 = 100 \text{ atm} \\ C_p = 37.12 + 6.17 \times 10^{-3}T \quad \text{J/K} \cdot \text{mole} \end{cases}$$

$$\Delta H_{(1)} \cong (7.1 \times 10^{-3})[1 - (3 \times 10^{-5}) \times 298] \times (100 - 1) = 0.696 \ atm \cdot liter = 71 \ J$$

$T_2 \leqq 301K$, $\triangle T \leqq 3K$, $\triangle H_{(2)} \approx \triangle H_{(1)}$

2. $S_T(P)$ $\quad dS = \left(\dfrac{\partial S}{\partial P}\right)_T dP + \left(\dfrac{\partial S}{\partial T}\right)_P dT$

$\quad$ constant T $\quad dS = \left(\dfrac{\partial S}{\partial P}\right)_T dP$

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

$$= -V\alpha dP$$

$$\therefore \Delta S = S(P_2, T) - S(P_1, T) = -\int_{P_1}^{P_2} V\alpha dP$$

* For condensed phase, $\triangle S \approx -V\alpha(P_2 - P_1)$

e.g. Fe, $T_1 = 298K$, $\quad P_1 = 1$ atm, $\quad P_2 = 100$ atm

$\triangle S_{(1)} \approx -0.0022$ J/K

$T_2 = 297.73K$, $\quad \triangle T = -0.27K$ $\quad \triangle S_{(2)} \approx \triangle S_{(1)}$

☆ $\because$H, S are insensitive to P for condensed phases.

$\quad \therefore$In materials applications, in which the pressure range is 0 to 1 atm, the influence of pressure on H and S of <u>condensed phases</u> can be ignored.

* For a closed system of fixed composition

$(T_1, P_1) \rightarrow (T_2, P_2)$

$$\Delta H = H(T_2, P_2) - H(T_1, P_1) = \int_{T_1}^{T_2} C_p dT + \int_{P_1}^{P_2} V(1 - \alpha T) dP$$

$$\Delta S = S(T_2, P_2) - S(T_1, P_1) = \int_{T_1}^{T_2} \frac{C_p}{T} dT - \int_{P_1}^{P_2} V \alpha dP$$

* constant P, T $\triangle G = \triangle H - T \triangle S$

$\therefore$ Equilibrium state at (T, P) can be determine

Ex1: $UF_4 + 2Mg \rightarrow 2MgF_2 + U$
   * exothermic reaction
   * $U_{(l)}$ anf $MgF_{2(l)}$ are immiscible
   * Starting reactunts $UF_4/Mg = 1:2$ (molar ratio)
   Adiabatic container 298K

Ask: 1. Can T_f be 1773 K?
        2. $T_f = ?$ composition of final products?

Given: $C_{p, U(\alpha)}$, $C_{p, U(\beta)}$, $C_{p, U(\gamma)}$, $C_{p, U(l)}$, $C_{p, MgF2(s)}$, $C_{p, MgF2(l)}$

   U: $T_{\alpha\beta} = 941$ K, $\triangle H_{\alpha\beta} = 2800$ J
       $T_{\beta\gamma} = 1049$ K, $\triangle H_{\beta\gamma} = 4800$ J
       $T_{mU} = T_{\gamma l} = 1408$ K, $\triangle H_{\gamma l} = \triangle H_{m,U} = 9200$ J

   MgF_2: $T_{m,MgF2} = 1536$ K, $\triangle H_{m,MgF2} = 58600$ J

        $H_{MgF2,298} = -1124200$ J/mole

        $H_{UF4,298} = -1919600$ J/mole

Sol: (1) Heat of reaction at 298 K, $\triangle H_{298}$

1. $\triangle H_{298} = (2H_{MgF2} + H_U) - (2H_{Mg} + H_{UF4})$

        $= 2 \times (-1124200) - (-1919600)$

        $= -328800$ J

   (2) Heat required to bring $(U + 2MgF_2)$ from 298K to 1773 K
   * U: 298 K $\rightarrow$ 1773 K, $\triangle H_1$

$$\Delta H_1 = \int_{298}^{T\alpha\beta} C_{p,U(\alpha)} dT + \Delta H_{\alpha\beta} + \int_{T\alpha\beta}^{T\beta\gamma} C_{p,U(\beta)} dT + \Delta H_{\beta\gamma} + \int_{T\beta\gamma}^{T\gamma l} C_{p,U(\gamma)} dT + \Delta H_{\gamma l}$$
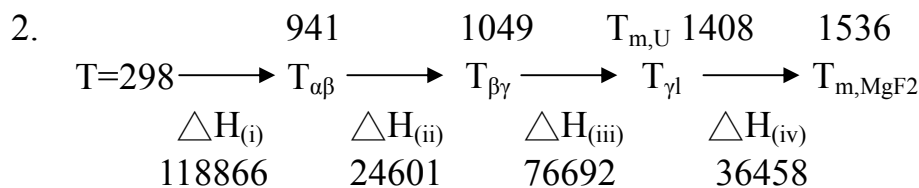
$$+ \int_{T_{\gamma l}}^{1773} C_{p,U(l)} dT = 76395 \ J$$

* 2 moles MgF_2: 298 K→1773 K, $\triangle H_2$

$$\Delta H2 = 2 \times [\int_{298}^{Tm,MgF2} C_{p,MgF2(s)} dT + \Delta H_m + \int_{Tm,MgF2}^{1773} C_{p,MgF2(l)} dT]$$

$$= 353696$$

$$\therefore \triangle H_{1773} = \triangle H_1 + \triangle H_2 = 430091 \ J$$

$$\because \triangle H_{1773} > | \triangle H_{298} | \quad \therefore 1773 \ K \ can \ not \ be \ attained$$

2.
$$\begin{array}{ccccc} & 941 & 1049 & T_{m,U} \ 1408 & 1536 \\ T=298 \longrightarrow & T_{\alpha\beta} \longrightarrow & T_{\beta\gamma} \longrightarrow & T_{\gamma l} \longrightarrow & T_{m,MgF2} \\ & \triangle H_{(i)} & \triangle H_{(ii)} & \triangle H_{(iii)} & \triangle H_{(iv)} \\ & 118866 & 24601 & 76692 & 36458 \end{array}$$

$$\therefore \triangle H_{1736} = \triangle H_{(i)} + \triangle H_{(ii)} + \triangle H_{(iii)} + \triangle H_{(iv)} = 256617 \ J$$

Heat remaining $Q = \triangle H_{298} + \triangle H_{1536} = -72183 \ J$

Assume x mole $MgF_{2(s)}$ melts

$$\therefore x \cdot \triangle H_{m,MgF2} = 72183$$

$$x = \frac{72183}{58600} = 1.23$$

$$\therefore \text{Final temp}, \ T_f = T_{m,MgF2} = 1536 \ K$$

Final composition: $U_{(l)} + MgF_{2(s)} + MgF_{2(l)} = (1 : 0.77 : 1.23)$

Note: 1. If $T_f = 1773$ K is required

Insufficient heat $Q = | \triangle H_{1773} | - | \triangle H_{298} | = 101291 \ J$
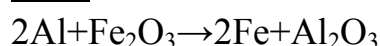
$$\therefore \int_{298}^{Ti} (\sum C_{p,reac\,tan\,ts}) dT = 101291$$

$$\int_{298}^{Ti} [2C_{p,Mg(s)} + C_{p,UF4}) dT = 101291$$

$$\therefore T_i = 859 \ K$$

prefect reactants to $T_i = 859$ K, then $T_f = 1773$ K

EX2: Thermit reaction

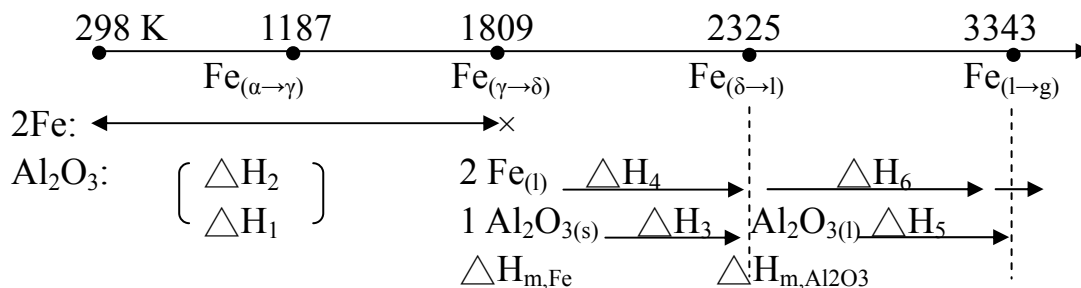$2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3$

adiabatic container at 298 K, $T_f = ?$ Composition=?

Given: H $_{Al2O3,298}$, $H_{Fe2O3,298}$

             $Cp_{Al2O3(s)}$, $Cp_{Fe(\alpha)}$, $Cp_{Fe(\gamma)}$, $Cp_{Fe(\delta)}$, $Cp_{Fe(l)}$, $Cp_{Al2O3(l)}$

$Fe_{(\alpha \to \gamma)}$, $\triangle H_{\alpha\gamma}=670$ T=1187 K
$Fe_{(\gamma \to \delta)}$, $\triangle H_{\gamma\delta}=840$ T=1664 K
$Fe_{(\delta \to l)}$, $\triangle H_{m,Fe}=13770$ T=1809 K
$Fe_{(l \to g)}$, $\triangle H_{b,Fe}=340159$ T=3343 K
$Al_2O_{3(s \to l)}$, $\triangle H_{m,Al2O3}=107000$, $T_{m,Al2O3}=2325$ K
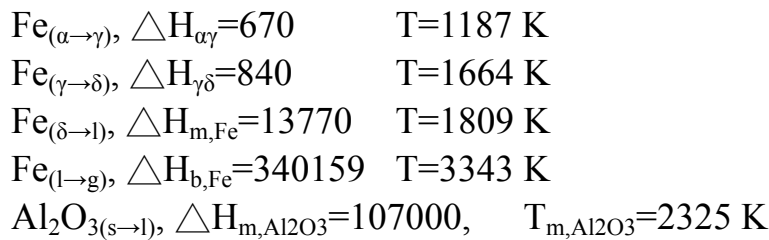
$\triangle H_{298}= H_{Al2O3,298} - H_{Fe2O3,298} = -852300$ J

$$\Delta H_1 = \int_{298}^{Tm,Fe} C_{p,Al2O3(s)} dT = 183649 \ J$$

$$\Delta H_2 = \left\{ 2 \int_{298}^{T\alpha\gamma} C_{p,Fe(\alpha)} dT + \Delta H_{\alpha\gamma} + \int_{T\alpha\gamma}^{T\gamma\delta} C_{p,Fe(\gamma)} dT + \Delta H_{\gamma\delta} + \int_{T\gamma\delta}^{Tm,Fe} C_{p,Fe(\delta)} dT + \Delta H_{m,Fe} \right\}$$

$$= 157541 \ J \qquad \Delta H_1 + \Delta H_2 = 341190 \ J$$

$$\Delta H_3 = \int_{Tm,Fe}^{Tm,Al2O3} C_{p,Al2O3(s)} dT = 71240 \ J$$

$$\Delta H_4 = 2[\int_{Tm,Fe}^{Tm,Al2O3} C_{p,Fe(l)} dT] = 43178 \ J \qquad \Delta H_3 + \Delta H_4 + \Delta H_{m,Al2O3} = 221418 \ J$$

$$\Delta H_5 = \int_{Tm,Al2O3}^{Tb,Fe} C_{p,Al2O3(l)} dT$$
$$\Delta H_6 = \int_{Tm,Al2O3}^{Tb,Fe} C_{p,Fe(l)} dT \qquad = 272600 \ J$$

$$\therefore \Delta H_{3343} = (\Delta H_1 + \Delta H_2) + (\Delta H_3 + \Delta H_4 + \Delta H_{m,Al2O3}) + (\Delta H_5 + \Delta H_6) = 835208 \ J$$

$$\therefore \Delta Q = \Delta H_{298} + \Delta H_{3343} = -17092 \ \Rightarrow \ boiling \ Fe_{(l)}$$

x moles $Fe_{(l)}$ boiling $\therefore x = \dfrac{\Delta Q}{\Delta H_{b,Fe}} = 0.05$

$\therefore$ $\begin{cases} T_f = T_{b,Fe} = 3343 \text{ K} \\ \text{composition: } Al_2O_{3(l)} + Fe_{(l)} + Fe_{(g)}: [1:1.95:0.05] \text{ moles} \end{cases}$

<u>Note:</u> If $T_f = T_{m,Fe} = 1809$ K $\Rightarrow$ Add. Fe

$\therefore \Delta Q' = \Delta H_{298} + (\Delta H_1 + \Delta H_2) = -511110 \ J$

y moles Fe(s) melts:

$y(\dfrac{\Delta H_2}{2}) = |\Delta Q'|$

y=6.49 moles

$\therefore$ starting $(Fe_{(s)} + Fe_2O_{3(s)} + Al_{(s)}) = (6.49:1:2)$ moles

<u>EX3:</u>

Supercooled 1mole $Sn_{(l)} \rightarrow Sn_{(s)}$ T=495 K, x=?mole solidified

Given: $\triangle H_m = 7070$ J, $T_m = 505$ K

$Cp_{(l)} = 34.7 - 9.2 \times 10^{-3}T$ J/K $\cdot$ mole

$Cp_{(s)} = 18.5 - 26 \times 10^{-3}T$ J/K $\cdot$ mole

<u>Sol:</u>

$T_m = 505K$ II $\rightarrow$ f

I ☐ IV

i

T=495K   III
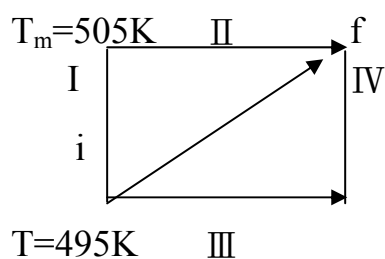
Final state: $\begin{cases} T = T_m = 505 \text{ K} \\ x \text{ mole } Sn_{(s)}, (1-x):Sn_{(l)} \end{cases}$

Adiabatic: $\triangle H = 0$

$\therefore \quad \Delta H = \Delta H_I = \Delta H_{II}$

$\Delta H_I = \int_{495}^{505} C_{p,Sn(l)} dT$

$\Delta H_{II} = x \cdot (-\Delta H_m)$

$\therefore -x \cdot \Delta H_m + \int_{495}^{505} C_{p,(l)} dT = 0$, $\quad x = 0.0426$

<或> $\Delta H = \Delta H_{III} + \Delta H_{IV} = 0$

$\Delta H_{IV} = x \cdot \int_{495}^{505} C_{p(s)} dT + (1-x) \int_{495}^{505} C_{p(l)} dT$

$-\Delta H_{III} = x \cdot \{\Delta H_m + \int_{505}^{495} [C_{p(l)} - C_{p(s)}] dT\}$