Examination # 1 Thermo

① Show that $\left(\frac{\partial C_p}{\partial P}\right)_T = -VT\left(\left(\frac{\partial \alpha}{\partial T}\right)_P + \alpha^2\right)$

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

dH exact differential $\Rightarrow \left(\frac{\partial C_p}{\partial P}\right)_T = \left(\frac{\partial\left(V - T\left(\frac{\partial V}{\partial T}\right)_P\right)}{\partial T}\right)_P$

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

$$\left(\frac{\partial C_p}{\partial P}\right)_T = V\alpha(\cancel{1} - \alpha T) - \cancel{V\alpha} - VT\left(\frac{\partial \alpha}{\partial T}\right)_P$$

$$\boxed{\left(\frac{\partial C_p}{\partial P}\right)_T = -VT\left(\alpha^2 + \left(\frac{\partial \alpha}{\partial T}\right)_P\right)}$$

② ⓐ Triple point defined by $P_s = P_\ell$

$$\Rightarrow 10.5916 - \frac{1871.2}{T} = 8.3186 - \frac{1425.7}{T}$$

$$\Rightarrow T_{\mathscr{t}} = 196\,K. \quad \rightarrow \log(P_{\mathscr{t}}) = 10.5916 - \frac{1871.2}{196}$$

$$P_{\mathscr{t}} = 10^{1.0447} = 11.08 \text{ torr.}$$

$$\boxed{\mathscr{t}\ (196\,K,\ 11.08 \text{ torr})}$$

(b) ΔH°_{fus} (close to triple point) = $\Delta H^\circ_{sub} - \Delta H^\circ_{vap}$

↑ ↑ calculated close to triple point

- solid $\rightleftharpoons$ vapor

$$K = \frac{P_s}{P^\circ} \quad \left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H^\circ_{sub}}{RT^2}$$

$$\Rightarrow \frac{d \ln P_s}{dT} = \frac{\Delta H^\circ_{sub}}{RT^2}$$

$$\log P_s(T) = 10.5916 - \frac{1871.2}{T}$$

$$\ln P_s(T) = \ln(10) \log P_s(T)$$

$$\Rightarrow \frac{d \ln P_s(T)}{dT} = (2.303)\frac{(1871.2)}{T^2} = \frac{\Delta H^\circ_{sub}}{RT^2}$$

$$\Rightarrow \Delta H^\circ_{sub} = (8.3145)(2.303)(1871.2)$$

$$\boxed{\Delta H^\circ_{sub} = 35.83 \text{ kJ/mol}}$$

- similarly liquid $\rightleftharpoons$ vapor.

$$\Delta H^\circ_{vap} = (8.3145)(2.303)(1425.7)$$

$$\boxed{\Delta H^\circ_{vap} = 27.30 \text{ kJ/mol}}$$

- $\Delta H^\circ_{fus} = (35.83 - 27.30)$ kJ/mol

$$\boxed{\Delta H^\circ_{fus} = 8.53 \text{ kJ/mol}}$$

① note all these values are positive

② note both ΔH°_{sub}, ΔH°_{vap} are >> ΔH_{fus}

(3) $PbO_{(s, red)} + CO_{(g)} \rightleftharpoons Pb_{(s)} + CO_{2(g)}$

(a) $\Delta_r G^\ominus = (-394.36 + 0) - (-188.93 - 137.17)$

$$\boxed{\Delta_r G^\ominus = -68.26 \text{ kJ/mol}}$$

$$\ln K_{298} = -\frac{\Delta_r G^\ominus}{RT} = +\frac{68.26\ 10^3}{8.314 \times 298} \Rightarrow$$

$$K_{298} = 9.2\ 10^{11}$$

(b) $$\frac{d \ln K}{dT} = \frac{\Delta_r H^\ominus(T)}{RT^2}$$

neglecting the Temp dependence of $\Delta_r H^\ominus$

$$\ln K_{400} - \ln K_{298} = -\frac{\Delta_r H^\ominus_{(298)}}{R}\left(\frac{1}{400} - \frac{1}{298}\right)$$

$$\Rightarrow \boxed{\ln K_{400} = 1.2\ 10^9}$$

$$\boxed{\Delta_r G^\ominus_{(400K)} \simeq -69.5 \text{ kJ/mol}}$$

(c) $$K = \frac{n_{CO_2}/n_T}{n_{CO}/n_T} = 9.2\ 10^{11}$$

$n_{CO_2} \simeq 1$

$$n_{CO} \simeq \frac{1}{9.2\ 10^{11}} = \underline{\underline{1.08\ 10^{-12}}}$$

④

- $dU = C_v dT + \left(T\left(\frac{\partial P}{\partial T}\right)_V - P\right) dV$

  $dU = T dS - P dV$

  $$\Rightarrow \boxed{dS = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV}$$

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

  $dH = T dS + V dP$

  $$\Rightarrow \boxed{dS = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP}$$

- at cst V : increase in T $\quad \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T}$

  $$\Rightarrow \boxed{T \uparrow \quad S \uparrow}$$

- at cst P : increase in T $\quad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$

  $$\Rightarrow \boxed{T \uparrow \quad S \uparrow}$$

- at cst T : increase in P $\quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P < 0$

  ↑ also Maxwell.

  $$\boxed{P \uparrow \quad S \downarrow}$$

- at cst T phase transition (CZTN)

  $dS = \frac{dH}{T}$ $\quad$ CZTN exothermic. $dH < 0$

  $\Rightarrow S \downarrow$

- at cst T increase in V $\quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V > 0$

  $$\boxed{V \uparrow \quad S \uparrow}$$