

# Maths 4 - Answers

$$\begin{aligned} a). f(x) \quad \left( \frac{\partial f(x)}{\partial x} \right)_y &= \frac{1}{x} \left( \frac{\partial f}{\partial x} \right)_y + f(x) \cdot \frac{\partial}{\partial x} \left( \frac{1}{x} \right) = \\ &= \frac{1}{x} \left( \frac{\partial f}{\partial x} \right)_y + f(x) \cdot \frac{-1}{x^2} \\ &= \frac{1}{x} \left( \frac{\partial f}{\partial x} \right)_y - \frac{f}{x^2} \end{aligned}$$

$$b). z(x,y) \rightarrow \text{total diff:} \quad dz = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy$$

$$c). z(x,y) = x^4 e^{3y}$$

$$\left( \frac{\partial z}{\partial x} \right)_y = 4x^3 e^{3y}$$

$$\left( \frac{\partial z}{\partial y} \right)_x = x^4 \cdot 3 \cdot e^{3y}$$

$$\begin{aligned} d). \frac{\partial^2 z}{\partial x \partial y} &= \left( \frac{\partial}{\partial x} \left( \frac{\partial z}{\partial y} \right)_x \right)_y = \frac{\partial}{\partial x} (x^4 \cdot 3 \cdot e^{3y})_y = 4x^3 \cdot 3 \cdot e^{3y} \\ &= 12x^3 e^{3y} \end{aligned}$$

$$\begin{aligned} \frac{\partial^2 z}{\partial y \partial x} &= \left( \frac{\partial}{\partial y} \left( \frac{\partial z}{\partial x} \right)_y \right)_x = \frac{\partial}{\partial y} (4x^3 e^{3y})_x = 4x^3 \cdot 3 \cdot e^{3y} \\ &= 12x^3 e^{3y} \end{aligned}$$

$$\text{So: } \frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x} \text{ as required.}$$

# Answers - Problem set 4

16)  $n = 1.0$ ,  $T_1 = 298 \text{ K}$ ,  $p_1 = 5 \text{ bar}$

a) isothermal  $\rightarrow dT = 0$ , reversible,  $p_2 = 1 \text{ bar}$   
 expansion  $\rightarrow v_1 \rightarrow v_2$ ,  $v_2 > v_1$

- $T_2 = T_1 = 298 \text{ K}$  (isothermal)

- work:  $dw_{rev} = -pdv$  ( $p = p_{ex}$ ; reversible)

$$= -\frac{nRT}{v} dv = -\frac{RT}{v} dv$$

$$W = -\int_{v_1}^{v_2} \frac{RT}{v} dv = -RT \ln \frac{v_2}{v_1} = -RT \ln \frac{p_1}{p_2} = +RT \ln \frac{p_2}{p_1}$$

$$W = 0.314 \cdot 298 \ln \frac{1}{5} = -4.0 \text{ kJ. (syst. does work on surr.)}$$

- $U_{pg} = \frac{3}{2} nRT \Big|_{n=1} = \frac{3}{2} RT \rightarrow$  only  $f(T)$ , but isothermal. So  $U$  does not change.

$$\rightarrow \Delta U = 0$$

- $du = dq + dw$

$$du = 0 \rightarrow dq = -dw = \frac{RT}{v} dv \quad (\text{or } q = -w)$$

$$q = -w = -RT \ln \frac{p_2}{p_1} = +4.0 \text{ kJ.}$$

- $ds = \frac{dq_{rev}}{T} \rightarrow \Delta S = \int \frac{dq_{rev}}{T} = \frac{q}{T} = \frac{4 \cdot 10^3}{298} = 13.4 \text{ J K}^{-1}$

- $A = U - TS \rightarrow$  at const  $T$ :  $dA = dU - TdS$  ( $-SdT = 0, u \text{ and } T = \text{const}$ )

$$\left. \begin{array}{l} \text{or } \Delta A = \Delta U - T\Delta S \\ \Delta U = 0 \end{array} \right\} \Delta A = 0 - 298 \cdot 13.4 = -4.0 \text{ kJ}$$

- $G = H - TS \xrightarrow{\text{at } T} \Delta G = \Delta H - T\Delta S$  or  $dG = dH - TdS$

$$\text{but } H = U + pV \rightarrow dH = dU + d(pV) = dU + d(nRT) = 0 + 0 = 0$$

$$\text{as } \Delta H = 0: \Delta G = -T\Delta S = -298 \cdot 13.4 =$$

$$\Delta G = -4.0 \text{ kJ.}$$

b) irreversible processes: cst. ext pressure  $p_{\text{ex}} = 1.0 \text{ bar}$   
 $\rightarrow$  still isothermal and same final pressure.  
 $\rightarrow$  state functions are indep. of the path, so will be the same as in a):

$$\left. \begin{array}{l} \bullet T_2 = T_1 = 298 \text{ K} \\ \bullet \Delta U = 0 \\ \bullet \Delta S = 13.4 \text{ J K}^{-1} \\ \bullet \Delta A = -4.0 \text{ kJ} \\ \bullet \Delta G = -4.0 \text{ kJ} \end{array} \right\} \text{all state functions}$$

non-state-functions:  $w$  &  $q$  (to be calculated in c))

c) isothermal:  $dT = 0$   $p_i = 5 \text{ bar}$   $p_f = p_{\text{ext}} = 1 \text{ bar}$ ,  $n = 1$   
 $\hookrightarrow$  constant during process

irreversible work:

$$\begin{aligned} w &= - \int_{v_1}^{v_2} p_{\text{ex}} dv = - p_{\text{ex}} \int_{v_1}^{v_2} dv = - p_{\text{ex}} (v_2 - v_1) = - p_2 (v_2 - v_1) \\ &= - p_2 \left( \frac{nRT}{p_2} - \frac{nRT}{p_1} \right) \stackrel{n=1}{=} - RT \left( \frac{p_2}{p_2} - \frac{p_2}{p_1} \right) \\ &= - RT \left( 1 - \frac{p_2}{p_1} \right) = - 0.314 \cdot 298 \left( 1 - \frac{1.0}{5.0} \right) = \end{aligned}$$

$$w = -2.0 \text{ kJ}$$

as  $\Delta U = 0$  (see b),  $q = -w$  ( $\Delta U = q + w$ )

$$\therefore q = +2.0 \text{ kJ}$$

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$$a) \cdot du = dq_{rev} + dw_{rev} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} du = dq - pdv + \mu dn$$

$$dw_{rev} = -pdv + \mu dn \quad (p = p_{ex} \leftrightarrow \text{reversible in deriving})$$

fundamental equations

$$ds = \frac{dq_{rev}}{T} \rightarrow Tds = dq_{rev} \rightarrow \text{sub in 1st Law}$$

$$(1) du = Tds - pdv + \mu dn \quad [\text{fund. eq. for } u]$$

$$\cdot G = H - TS = u + pv - TS \quad (H = u + pv)$$

$$dg = du + pdv + vdp - Tds + SdT$$

sub in eq. (1)  $\rightarrow$

$$dg = \cancel{Tds} - \cancel{pdv} + \mu dn + \cancel{pdv} + vdp - \cancel{Tds} - SdT$$

$$dg = -SdT + vdp + \mu dn \quad [\text{Fund. Eq. for } G]$$

$$b) dg = \left( \frac{\partial G}{\partial T} \right)_{p,n} dT + \left( \frac{\partial G}{\partial p} \right)_{T,n} dp + \left( \frac{\partial G}{\partial n} \right)_{T,p} dn$$

by comparison  $-S$   $v$   $\mu$

to F.E. for G:

$$\Rightarrow -S = \left( \frac{\partial G}{\partial T} \right)_{p,n}$$

$$c) \left( \frac{\partial (G/T)}{\partial T} \right)_{p,n} = \frac{1}{T} \left( \frac{\partial G}{\partial T} \right)_{p,n} + G \left( \frac{-1}{T^2} \right) =$$

$-S$   $H-TS$

$$= \frac{1}{T} \cdot (-S) - \frac{H}{T^2} + \frac{TS}{T^2} = -\frac{H}{T^2}$$

$$\therefore \left( \frac{\partial (G/T)}{\partial T} \right)_{p,n} = -\frac{H}{T^2}$$

$$\Delta H = 1.0961 \text{ kJ mol}^{-1}$$

$$(18) T = 298 \text{ K} \quad G \rightarrow D \quad \Delta S = -3.2552 \text{ J K}^{-1} \text{ mol}^{-1}$$

a) spontaneous or not?  $\rightarrow$  at  $\text{cst } T \text{ \& } P^\ominus$ . consider Gibbs:  $\Delta G$

$$\text{@ cst } T: G = H - TS \xrightarrow{\text{cst } T} \Delta G = \Delta H - T\Delta S$$

$$\Delta G = 1.0961 \cdot 10^3 - 298 \cdot (-3.2552) = +2.07 \text{ kJ mol}^{-1}$$

$\Delta G > 0 \rightarrow$  not spontaneous, so  $D \rightarrow G$  transition is spontaneous at  $P = P^\ominus$

b)  $\Delta G = \Delta H - T\Delta S \rightarrow$  as  $T \uparrow$ , the  $-T\Delta S$  term becomes <sup>more</sup> dominant. because  $-T\Delta S$ -term  $> 0$  ( $\Delta S < 0$ ), an increasing  $T$  leads to an increase of  $\Delta G$  for the  $G \rightarrow D$  transition

c) Fund. eq.  $G$ :  $dg = -SdT + Vdp + \mu dn$  <sup>(not req.)</sup>  $\rightarrow \left(\frac{\partial G}{\partial P}\right)_{T,n} = V$

$$\int_{G(P_1)=G(P^\ominus)}^{G(P_2)} dg = V \int_{P_1=P^\ominus}^{P_2} dp \rightarrow G(P_2) = G(P_1) + V(P_2 - P_1) \quad \left. \begin{array}{l} P_2 = P \\ P_1 = P^\ominus \end{array} \right\}$$
$$G(P) = G(P^\ominus) + V(P - P^\ominus)$$

$$\text{so: } G_D(P) = G_D^\ominus + V_D(P - P^\ominus) \quad \& \quad G_G(P) = G_G^\ominus + V_G(P - P^\ominus)$$

$$d) \Delta V = V_D - V_G = -1.92 \cdot 10^{-6} \text{ m}^3 \text{ mol}^{-1}, \quad \Delta G^\ominus = \frac{2.07 \cdot 10^3 \text{ J mol}^{-1}}{2.07 \cdot 10^3 \text{ J mol}^{-1}}$$

@ equilibrium:  $\Delta G = 0 \quad \Delta G = G_D - G_G$  (fill in from c):

$$\Delta G = G_D^\ominus + V_D(P - P^\ominus) - [G_G^\ominus + V_G(P - P^\ominus)] =$$

$$= \Delta G^\ominus + (V_D - V_G)(P - P^\ominus) = \Delta G^\ominus + \Delta V(P - P^\ominus) = 0$$

$$\Rightarrow P = P^\ominus - \frac{\Delta G^\ominus}{\Delta V} = 1 \cdot 10^5 - \frac{2.07 \cdot 10^3 \text{ J mol}^{-1}}{-1.92 \cdot 10^{-6} \text{ m}^3 \text{ mol}^{-1}} = 1.49 \cdot 10^9 \text{ Pa}$$

$$P \approx 15000 \times P^\ominus !!$$

(note:  $\Delta_r G = \Delta_r G^\ominus$  as:  $\Delta_r G = \Delta_r G^\ominus + RT \ln K_p$ , but for solid  $\rightleftharpoons$  solid  $K_p = \frac{1}{1} = 1 \quad \ln K_p = 0 \rightarrow \Delta_r G = \Delta_r G^\ominus$ )  
 $\Rightarrow$  see chemical equilibrium, lecture 5 & 6

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a)  $dA = -SdT - pdV + \mu dn$

$$= \underbrace{\left(\frac{\partial A}{\partial T}\right)_{V,n}}_{-S} dT + \underbrace{\left(\frac{\partial A}{\partial V}\right)_{T,n}}_{-p} dV + \underbrace{\left(\frac{\partial A}{\partial n}\right)_{T,V}}_{\mu} dn$$

→ so:  $\left(\frac{\partial S}{\partial V}\right)_{T,n} = \frac{\partial}{\partial V} (S)_{T,n} = \frac{\partial}{\partial V} \left(-\left(\frac{\partial A}{\partial T}\right)_{V,n}\right)_{T,n}$

↑  
tot. diff! order of diff. is arbitrary.

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_{T,n} = \frac{\partial}{\partial T} \underbrace{\left(-\left(\frac{\partial A}{\partial V}\right)_{T,n}\right)_{V,n}}_p =$$

$$= \left(\frac{\partial p}{\partial T}\right)_{V,n} \Rightarrow \left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial p}{\partial T}\right)_{V,n} \checkmark$$

b) p.g. →  $pV = nRT \rightarrow p = \frac{nRT}{V} \quad V_2 = 2V_1$

for p.g.:  $\left(\frac{\partial p}{\partial T}\right)_{V,n} = \frac{nR}{V}$

⇒ so from Maxwell relation:  $\left(\frac{\partial S}{\partial V}\right)_{T,n} = \frac{nR}{V}$

$$\int_{S(V_1)}^{S(V_2)} dS = nR \int_{V_1}^{V_2=2V_1} \frac{1}{V} dV = nR \ln \frac{V_2}{V_1} = nR \ln 2$$

⇒  $\Delta S = nR \ln 2$

(20)

a) atomic p.g.  $U = \frac{3}{2}nRT$ ,  $n=1.0$

$C_p = A + BT + CT^2$ , but also  $C_p = \left(\frac{\partial H}{\partial T}\right)_p$

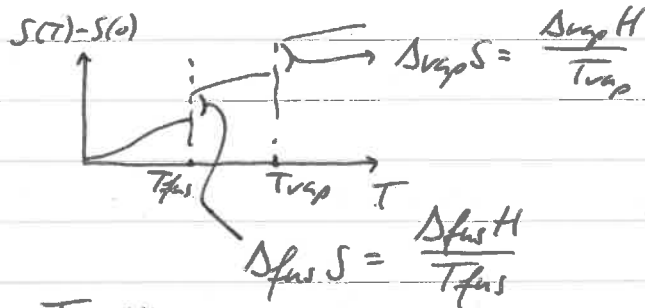
for p.g.:  $H = U + pV = U + nRT = \frac{3}{2}RT + RT = \frac{5}{2}RT$   
 $\uparrow$   
 $n=1.0$

$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \frac{\partial}{\partial T} \left(\frac{5}{2}RT\right) = \frac{5}{2}R$

so  $C_p \neq C_p(T) \rightarrow \frac{5}{2}R = A + \underbrace{BT + CT^2}_{=0} \rightarrow B=C=0$

$A = \frac{5}{2}R = 20.79 \text{ J mol}^{-1} \text{ K}^{-1}$  ( $A = C_p$ )

b) recall from lecture:



$T_{fus} = \text{melting!}$

now: consider  $T_{fus} = T_{melting}$ , at some p.  
where the melt (liquid) and solid are in equilibrium

- entropy (see graph):  $\Delta_{fus} S \neq 0 \rightarrow$  not the same in (s) & (l).
- chemical potential: yes, is the same in (l) & (s) at  $T = T_{fus}$  at and at p.

$\rightarrow$  there is chemical equilibrium between (s) & (l):  
 $\mu(s) = \mu(l)$ .  $\Delta\mu = 0$ .

- enthalpy:  $\Delta_{fus} H \neq 0 \rightarrow$  not the same in (l) & (s).  
 $\hookrightarrow$  see also graph ( $\Delta_{fus} S = \frac{\Delta_{fus} H}{T_{fus}}$ )

- Gibbs:  $\Delta_{fus} G = 0$ , equilibrium  
at given p & T  $\rightarrow$  also  $G_m = \mu = \frac{G}{n}$ , so as  $\mu(s) = \mu(l)$   
 $\Delta G = 0$ .  $\rightarrow$  so yes, same in (l) & (s)

- Helmholtz:  $\Delta A = 0$ , equilibrium at constant T & V  
as here we have at T & p  $\rightarrow \Delta A \neq 0$ . not same in (l) & (s)

c)  $T = T_{\text{trap}} \rightarrow$  equilibrium between (l) & (g)  $\rightarrow \Delta G = 0$

$$G = H - TS \rightarrow \Delta G = \Delta H - T \Delta S \text{ @ cst } T (T = T_{\text{trap}})$$

$$\Delta G = 0 \rightarrow \Delta_{\text{trap}} S = \frac{\Delta_{\text{trap}} H}{T_{\text{trap}}} = \frac{98.01 \cdot 10^3}{1156} = 84.78 \text{ J mol}^{-1} \text{ K}^{-1}$$

d) we need to "integrate up" from  $S(0)$  up to  $T$  of interest:  
(lot of work)

$$\begin{aligned} \text{general eqn: } S(T) = S(0) &+ \int_0^{T_{\text{fus}}} \frac{C_p(s)}{T} dT + \frac{\Delta_{\text{fus}} H}{T_{\text{fus}}} \\ &+ \int_{T_{\text{fus}}}^{T_{\text{trap}}} \frac{C_p(l)}{T} dT + \frac{\Delta_{\text{trap}} H}{T_{\text{trap}}} \\ &+ \int_{T_{\text{trap}}}^T \frac{C_p(g)}{T} dT. \end{aligned}$$

Here: ignore contributions ~~but~~  $T < 10 \text{ K} \rightarrow$  so lower limit = 10 K.  
•  $T$  of interest is 1000 K, so  $T < T_{\text{trap}}$ , so only (s) & (l):

$$S(T) = S(0) + \int_{10}^{T_{\text{fus}}} \frac{C_p(s)}{T} dT + \frac{\Delta_{\text{fus}} H}{T_{\text{fus}}} + \int_{T_{\text{fus}}}^{1000} \frac{C_p(l)}{T} dT$$

$\Rightarrow S(0) = 0$  &  $C_p = A + BT + CT^2 \rightarrow C_p = C_p(T)!$

$$\begin{aligned} S(T) = &\int_{10}^{T_{\text{fus}}} \left( \frac{A(s)}{T} + B(s) + C(s)T \right) dT + \frac{\Delta_{\text{fus}} H}{T_{\text{fus}}} + \\ &\int_{T_{\text{fus}}}^{1000} \left( \frac{A(l)}{T} + B(l) + C(l)T \right) dT = \end{aligned}$$

$$= \left[ A(s) \ln T + B(s)T + \frac{1}{2}C(s)T^2 \right]_{10}^{T_{\text{fus}}} + \frac{\Delta_{\text{fus}} H}{T_{\text{fus}}} + \left[ A(l) \ln T + B(l)T + \frac{1}{2}C(l)T^2 \right]_{T_{\text{fus}}}^{1000}$$



$$S(T) = \left[ A(s) \ln T + B(s)T + \frac{1}{2} C(s) T^2 \right]_{10}^{T_{fus}} + \frac{\Delta_{fus} H}{T_{fus}} + \left[ A(l) \ln T + B(l)T + \frac{1}{2} C(l) T^2 \right]_{T_{fus}}^{1000} \quad (\text{copy from prev. page})$$

⇒ now filling in all values:

		solid	liquid	
$T_{fus} = 371.0 \text{ K}$	A	72.6	40.3	$\text{J mol}^{-1} \text{K}^{-1}$
$\Delta_{fus} H = 2.601 \cdot 10^3 \text{ J mol}^{-1}$	B	$-9.49 \cdot 10^{-3}$	$-20.2 \cdot 10^{-3}$	$\text{J mol}^{-1} \text{K}^{-2}$
	C	$-731 \cdot 10^{-6}$	$20.7 \cdot 10^{-6}$	$\text{J mol}^{-1} \text{K}^{-3}$

$$\Rightarrow S(T) = S(T = 1000 \text{ K})$$

$$= 208.65 + 7.01 + 31.15 = 246.8 \text{ J mol}^{-1} \text{K}^{-1}$$