

### Maths (3)

$$a) \int_{x_1}^{x_2} \left( \frac{a}{x} + b + cx \right) dx = \left[ a \ln x + bx + \frac{1}{2} cx^2 \right]_{x_1}^{x_2} = \\ = a \ln \frac{x_2}{x_1} + b(x_2 - x_1) + \frac{1}{2} c(x_2^2 - x_1^2).$$

$$b) \frac{(T_1 + T_2)^2}{4T_1 T_2} = \frac{T_1^2 + T_2^2 + 2T_1 T_2}{4T_1 T_2} = \\ = \frac{T_1^2 + T_2^2 + 4T_1 T_2 - 2T_1 T_2}{4T_1 T_2} = \frac{4T_1 T_2}{4T_1 T_2} + \frac{T_1^2 + T_2^2 - 2T_1 T_2}{4T_1 T_2} = \\ = 1 + \frac{(T_1 - T_2)^2}{4T_1 T_2}$$

$$c) \left( \frac{\partial f}{\partial x} \right)_y = \frac{\partial}{\partial x} (hy^2 x^2 \ln(gx))_y \stackrel{\text{product \& chain rule}}{=} hy^2 x^2 \frac{1}{gx} \cdot g + hy^2 2x \ln(gx) = \\ = hy^2 x + 2hy^2 x \ln(gx) = hy^2 x (1 + 2 \ln(gx)).$$

(or a diff. variation of this).

$$d) \frac{3}{2} \int_{T_1}^{T_2} \frac{1}{T} dT = - \int_{v_1}^{v_2} \frac{1}{v} dv \rightarrow \frac{3}{2} \ln \frac{T_2}{T_1} = - \ln \frac{v_2}{v_1} \\ \rightarrow \ln \left( \frac{T_2}{T_1} \right)^{3/2} = \ln \frac{v_1}{v_2} \Rightarrow \frac{v_1}{v_2} = \left( \frac{T_2}{T_1} \right)^{3/2}.$$

[so using  $a \ln b = \ln b^a$ ].

# Answers - problem set 3

11.

a) i.  $dS \geq \frac{dq}{T}$  or  $dS = \frac{dq_{rev}}{T}$

ii.  $S = k_B \ln W$

b) 2<sup>nd</sup> Law:  $\Delta S_{total} > 0$  for spontaneous change

c)  $l \rightarrow s$ :  $\Delta S_{syst} < 0$  (freezing),

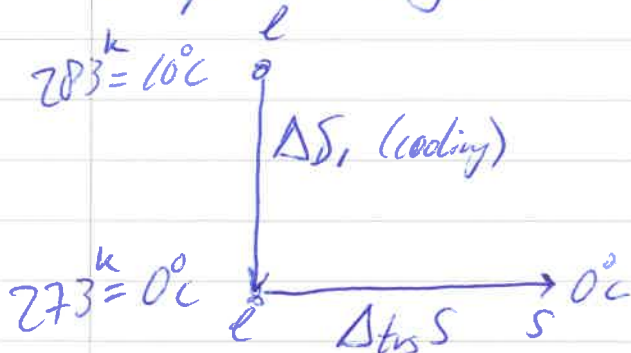
but  $\Delta_{freeze} H^\circ = -6 \text{ kJ mol}^{-1} < 0$ : exothermic, so heat transfer to surroundings:

therefore  $\Delta S_{surr} = \int \frac{dq_{surr}}{T_{surr}} > 0$

and  $|\Delta S_{surr}| > |\Delta S_{syst}| \rightarrow \Delta S_{tot} > 0$

(if  $T_{surr}$  is low enough)

d)  $C_p = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta_{fus} H^\circ = 6 \text{ kJ mol}^{-1}$ ,  $n = 1$



$$\Delta S_{tot} = \Delta S_l + \Delta S_{tr} S$$

$$= \int_{273}^{203} \frac{dq_{cool}}{T} + \int \frac{dq_{tr}}{T_{tr}}$$

$P = P^\circ$  (not given, but freezing @  $0^\circ\text{C}$ )  $\uparrow$   $\int \frac{dq_{cool}}{T} + \int \frac{dq_{tr}}{T_{tr}} =$

$$\Delta S_{tot} = \int_{273}^{203} \frac{C_p}{T} dT + \frac{\Delta H^\circ}{T_{tr}} = C_p \ln \frac{273}{203} - \frac{\Delta_{fus} H^\circ}{T_{tr}} =$$

$$= 75.3 \ln \left( \frac{273}{203} \right) - \frac{6000}{273} = -24.7 \text{ J K}^{-1}$$

e). cooling: water m/c loose Flain

freezing: m/c from liq  $\rightarrow$  solid, more ordered.

$\Rightarrow$  both processes decrease "disorderliness"  
of system  $\rightarrow \Delta S_{tot} < 0$ .

(12) a).  $Ne(g) \rightarrow$  atomic p.g.  $\rightarrow U = \frac{3}{2} nRT$

$$C_v = \left( \frac{\partial U}{\partial T} \right)_v = \frac{\partial}{\partial T} \left( \frac{3}{2} nRT \right) = \frac{3}{2} nR$$

$$n=1 \rightarrow C_v = \frac{3}{2} R$$

$$S_m(T_1 = 298K) = 146.22 \text{ J K}^{-1}$$

heating or increase in  $T$  @ cst  $v$ :

$$dU_{rev} = -p_{ext} dV = 0 \quad \begin{array}{l} dV=0 \\ \downarrow \end{array}$$

$$\left. \begin{array}{l} dU = dq_{rev} \\ = C_v dT \end{array} \right\} \begin{array}{l} dS = \frac{C_v}{T} dT \\ \int_{S(T_1)}^{S(T_2)} dS = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_v}{T} dT \end{array}$$

$$S_m(T_2 = 500K) = S_m(T_1 = 298K) + C_v \ln \frac{T_2}{T_1}$$

$$= 146.22 + \frac{3}{2} R \ln \frac{500}{298}$$

$$= 152.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

b)  $n=3$   $T_1=298\text{K}$  &  $T_2=1098\text{K}$   $p=1\text{atm}$

$$C_p = a + bT + cT^2$$

$$a = 23.64$$

$$b = 4.79 \cdot 10^{-2}$$

$$c = 7.93 \cdot 10^{-5}$$

heating @ const P:

$$dS = \frac{dq_{\text{rev}}}{T} \stackrel{\text{const } P}{=} \frac{dH}{T} = \frac{C_p}{T} dT$$

$$\int_{S(T_1)}^{S(T_2)} dS = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_p}{T} dT, \quad C_p = C_p(T)!$$

$$\Delta S = \int_{T_1}^{T_2} \left( \frac{a}{T} + b + cT \right) dT =$$

$$= \left[ a \ln T + bT + \frac{1}{2} cT^2 \right]_{T_1}^{T_2} =$$

$$= a \ln \frac{T_2}{T_1} + b(T_2 - T_1) + \frac{1}{2} c(T_2^2 - T_1^2) =$$

$$= 58.4 \text{ J K}^{-1} \text{ mol}^{-1} \rightarrow n=3 : \Delta S = 175 \text{ J K}^{-1}$$

c)  $n=2$ , p.g.,  $dT=0$   $V_A \rightarrow V_B$

$$dU=0 \rightarrow dq_{\text{rev}} = -dw_{\text{rev}} = \int_{V_A}^{V_B} p dV = \frac{nRT}{V} dV$$

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = \int_{V_A}^{V_B} \frac{nRT}{VT} dV = nR \ln \frac{V_B}{V_A}$$

$$5.595 = 2R \ln \frac{V_B}{V_A} \rightarrow \frac{V_B}{V_A} = 1.4$$

(as  $S$  = state function we can do calculation reversibly)

13 a)  $dS = \frac{dq_{rev}}{T}$  (see Q. 12 c).

$$dS = \frac{dq_{rev}}{T} = \frac{-dw_{rev}}{T} = \frac{pdv}{T} = \frac{nRT}{TV} dv$$

$du=0$  (isothermal exp. p.g.)

$$v_2 = 2v_1$$

$$\Delta S = \int_{v_1}^{v_2} nR \cdot \frac{1}{v} dv = nR \ln \frac{v_2}{v_1} = nR \ln 2$$

b)  $\Delta S = nR \ln 2 = S_2 - S_1$

$\boxed{nR = Nk_B}$

$$Nk \ln 2 = k \ln w_2 - k \ln w_1$$

$$k \ln 2^N = k \ln \frac{w_2}{w_1}$$

$$\overset{\circ}{\partial} \rightarrow \frac{w_2}{w_1} = 2^N$$

$N$  molecules  $\rightarrow$  per molecule the number of ways to realise the given configuration doubles:

ej.  $N=1$   $\frac{w_2}{w_1} = 2$  as  $v_2 = 2v_1$ !

for  $N$  mole  $\rightarrow 2 \cdot 2 \cdot 2 \cdots 2 = 2^N$

$\rightarrow$  so number of ways to realise given config increases by factor  $2^N$ .

(14)



$$T_2 > T_1, \quad p = \text{cst.}$$

$T_f = \text{final temp}$

a).  $-q_{1 \rightarrow 2} = q_{2 \rightarrow 1}$  (no heat loss to surr.).

$$-dq_{1 \rightarrow 2} = dq_{2 \rightarrow 1} \quad \& \text{ as } p = \text{cst} : dq_p = c_p dT$$

So:  $-q_{12} = q_{21}$

$$-\int_{T_1}^{T_f} c_p dT = \int_{T_2}^{T_f} c_p dT \quad \text{for}$$

$$-c_p (T_f - T_1) = c_p (T_f - T_2)$$

$$-T_f + T_1 = T_f - T_2 \rightarrow 2T_f = T_1 + T_2$$

$$\Rightarrow T_f = \frac{1}{2} (T_1 + T_2)$$

b).  $\Delta S = \Delta S_1 + \Delta S_2 = \int_{T_1}^{T_f} \frac{c_p dT}{T} + \int_{T_2}^{T_f} \frac{c_p dT}{T}$

$$= c_p \ln \frac{T_f}{T_1} + c_p \ln \frac{T_f}{T_2} =$$

$$= c_p \ln \left( \frac{T_f^2}{T_1 T_2} \right)$$

Note: not final temp

c) 2<sup>nd</sup> Law for spont. proc:  $\Delta S_{tot} > 0$

from b):  $\Delta S_{tot} = C_p \ln \frac{T_f^2}{T_1 T_2}$  } sub in T<sub>f</sub>:

from a):  $T_f = \frac{1}{2}(T_1 + T_2)$

$$\Delta S = C_p \ln \left\{ \frac{(T_1 + T_2)^2}{4T_1 T_2} \right\} = C_p \ln \left\{ \frac{T_1^2 + T_2^2 + 2T_1 T_2}{4T_1 T_2} \right\}$$

tricky

$$= C_p \ln \left\{ \frac{T_1^2 - 2T_1 T_2 + T_2^2 + 4T_1 T_2}{4T_1 T_2} \right\} =$$

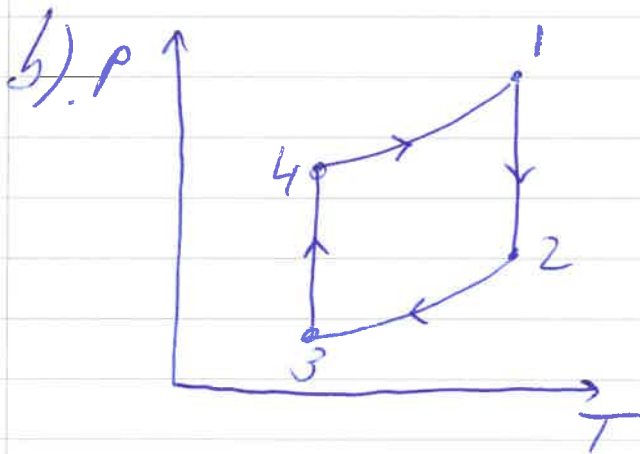
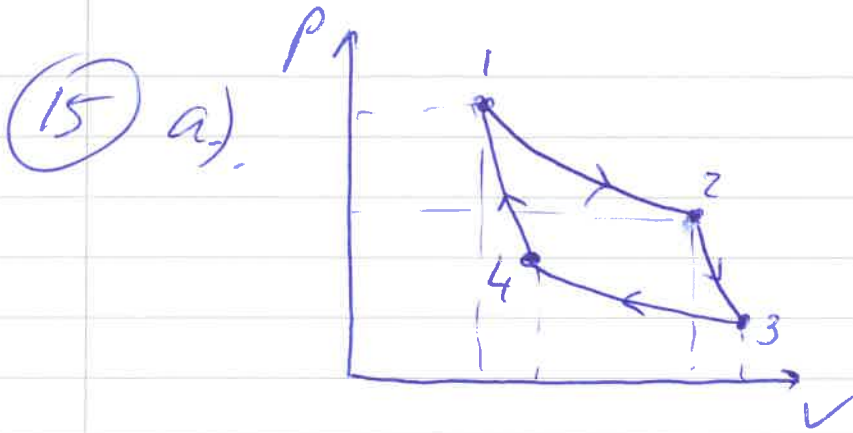
$$= C_p \ln \left\{ 1 + \frac{(T_1 - T_2)^2}{4T_1 T_2} \right\}$$

$$\text{as } \frac{(T_1 - T_2)^2}{4T_1 T_2} > 0 \rightarrow \Delta S > 0.$$

also: no heat exchange between syst. & surr:

$$\Delta S_{surr} = 0$$

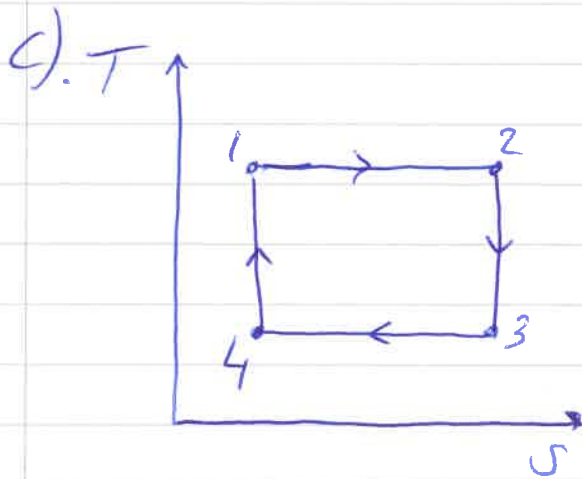
$$\begin{aligned} \therefore \Delta S_{tot} &= \Delta S + \Delta S_{surr} = C_p \ln \left( 1 + \frac{(T_1 - T_2)^2}{4T_1 T_2} \right) + 0 > 0 \checkmark \\ &= C_p \ln \left( 1 + \frac{(T_1 - T_2)^2}{4T_1 T_2} \right) + 0 > 0 \checkmark \end{aligned}$$



$$P_1 > P_2 > P_4 > P_3$$

$$T_1 = T_2 \quad \text{and} \quad T_3 = T_4$$

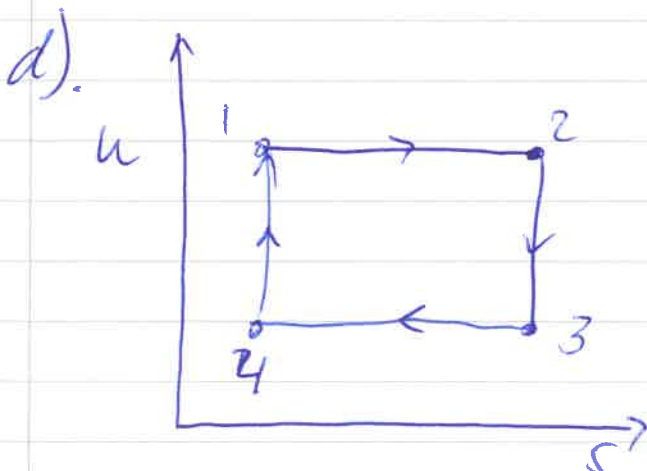
$$T_1 > T_3$$



$$T_1 = T_2 \quad \& \quad T_3 = T_4 \quad \& \quad T_1 > T_3$$

$$S_2 = S_3 \quad \& \quad S_1 = S_4$$

$$\& \quad S_1 < S_2$$



for perfect gas  $u = \frac{3}{2} nRT$   
 i.e.  $u \sim T$ , so  
 this will look as c).



