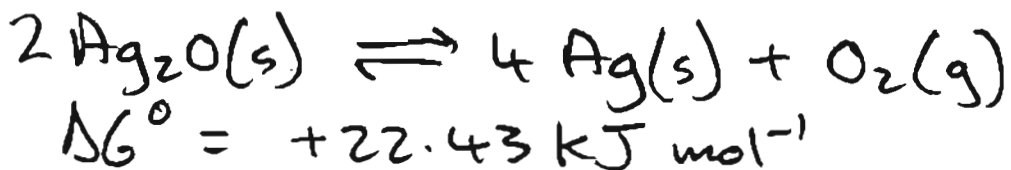


Q. Determine the equilibrium partial pressure of  $O_2(g)$  above a mixture of  $Ag(s)$  and  $Ag_2O(s)$  at 298 K



First, write out equilibrium constant expression

$$K = \frac{[Ag(s)]^4 \cdot P_{O_2(s)}}{[Ag_2O(s)]^2} = \frac{(1)^4 P_{O_2}}{(1)^2} = P_{O_2} = K_p$$

Then use  $\Delta G^\circ$  (given) to get a value for  $K_p$  ( $= P_{O_2}$ )  
want this

$$\Delta G^\circ = -RT \ln K ; K = e^{-\frac{\Delta G^\circ}{RT}}$$

$$K = e^{-\frac{22.43 \times 10^3}{8.314(298)}} = e^{-9.05}$$

$$K = \underline{\underline{1.17 \times 10^{-4} \text{ atm}}} \quad (= P_{O_2})$$

ADDITIONAL PROBLEMS 1

Q - continuing with  $\text{Ag}_2\text{O}$  - ...

At what temp. will the pressure of  $\text{O}_2$  above  $\text{Ag}_2\text{O}(s)$  become equal to

0.10 atm? Given  $\Delta H^\circ = +61.18 \text{ kJ mol}^{-1}$   
 $\Delta S^\circ = +0.13 \text{ kJ mol}^{-1}$

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Step 1. If  $P_{\text{O}_2} = 0.10 \text{ atm}$ , then  $K = K_p = 0.10$

Step 2 Use this value of  $K$  to get  $\Delta G^\circ$  at this new  $T$ .

$$\Delta G_T^\circ = -RT \ln K = -8.314(T) \ln 0.10 \\ = +19.1 \times 10^{-3}(T) \text{ kJ}$$

Step 3 OK, let's use the given values of  $\Delta H^\circ$  &  $\Delta S^\circ$  to get  $\Delta G_T^\circ$

$$\Delta G_T^\circ = \Delta H^\circ - T\Delta S^\circ = 61.18 - 0.13(T) \text{ kJ}$$

Step 4. Equating steps 2 & 3 (all kJ)

$$19.1 \times 10^{-3} T = 61.18 - 0.13 T$$

$$T = \underline{\underline{410.3 \text{ K}}}. \quad \text{or use Van't Hoff equ.}$$

Q Calculate the approx. temp. range over which the rx.

$2\text{NO}(g) + 2\text{CO}(g) \rightarrow 2\text{CO}_2(g) + \text{N}_2(g)$   
is spontaneous, when all reactants and products have partial P's of 1 atm.

Given:  $\Delta H_f^\circ$  and  $S^\circ$  for all compounds

$$\Delta H_{\text{rxn}}^\circ (\text{from } \Delta H_f^\circ \text{ values}) = -746.7 \text{ kJ} \quad (\text{favourable})$$

$$\Delta S_{\text{rxn}}^\circ (\text{from } S^\circ \text{ values}) = -198.1 \text{ J K}^{-1} \quad (\text{unfav.})$$

$$\Delta G_{\text{rxn}}^\circ(298) = -746.7 - (-198.1 \times 10^{-3} \times 298) \text{ kJ}$$

$$\Delta G_{\text{rxn}}^\circ = \underline{\underline{-687.7 \text{ kJ}}} \quad (\text{spont. @ } 298 \text{ K})$$

What about higher T's?

The rx. will be spont. under std. conditions up to the T at which,

$$\Delta H^\circ = T \Delta S^\circ$$

$$T = \frac{\Delta H_{\text{rxn}}^\circ}{\Delta S_{\text{rxn}}^\circ} = \frac{-746.7 \times 10^3 \text{ J}}{-198.1 \text{ J K}^{-1}} = 3769 \text{ K}$$

Above this T, the unfavourable entropy term in  $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$  dominates (making  $\Delta G^\circ$  +ve) so the rx. will not go forward. approx.  $3500^\circ\text{C}$

ADD. PROBS. 3

Q Dr Nick is at 5500 m on the N face of Kanchenjunga. His clothing has absorbed 1 kg of water and body warmth dries it.

- What heat loss does the body have to make good?
- How much glucose would have to be consumed to replace the loss?
- If the loss was not replaced, what would be the drop in temperature of Dr Nick?

Assume heat capacity is the same as that of water =  $75.2 \text{ J K}^{-1} \text{ mol}^{-1}$ .  $\Delta H_{\text{vap}}(\text{H}_2\text{O}) = 40.7 \text{ kJ mol}^{-1}$ ;  $\Delta H_{\text{comb}}(\text{C}_6\text{H}_{12}\text{O}_6) = -2802 \text{ kJ mol}^{-1}$ . Dr. Nick is 75 kg.

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a) Clothing has absorbed 1 kg of water =  $\frac{1000 \text{ g}}{18 \text{ g mol}^{-1}} = 55.5 \text{ mol}$

Heat required to vaporise this is  $q = \Delta H = 55.5 \text{ mol} \times 40.7 \text{ kJ mol}^{-1} = \underline{2258.9 \text{ kJ}}$

ADD. PROBS. 4

b) Dr. Nock has to replace this amount by chomping on some glucose.

1 mol glucose will give  $2802 \text{ kJ mol}^{-1}$

$$\therefore \text{he needs } \frac{2258.9 \text{ kJ}}{2802 \text{ kJ mol}^{-1}} = 0.81 \text{ mol glucose}$$

Molar mass glucose  $\approx 180 \text{ g}$ .

$$\therefore 0.81 \text{ mol} = \underline{145.8 \text{ g}} \text{ (yummy!)}$$

c) If the heat loss was not replaced

$$\Delta T = \frac{q}{n C_p} = \frac{2258.9 \times 10^3 \text{ J}}{\left( \frac{75 \times 10^3 \text{ g}}{18 \text{ g mol}^{-1}} \right) 75.2 \text{ J K}^{-1} \text{ mol}^{-1}}$$

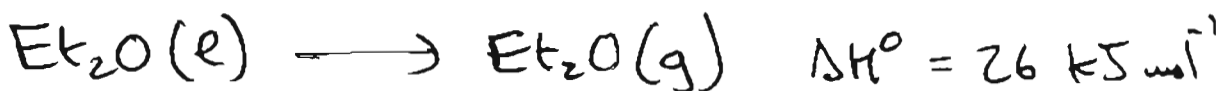
$$\Delta T = 7.2 \text{ K} = \underline{7.2^\circ \text{C}}$$

**HYPOTHERMIA CAN BE FATAL**

ADD. PROBS.  $\therefore$  you must know your calculations!!

Q

At the normal boiling point of ethyl ether,  $34.5^\circ\text{C}$ ,  $\Delta H^\circ$  of vap. =  $26.0 \text{ kJ mol}^{-1}$ . Calculate  $q, w, \Delta U, \Delta S^\circ, \Delta G$  &  $K$  for the vaporisation of 1 mole of ethyl ether.



Normal boiling pt. is the b.p. at  $P = 1 \text{ atm}$

$$\text{B.p.} = 273 + 34.5 = 307.5 \text{ K}$$

q At constant  $P$ ,  $q = \Delta H = \underline{26.0 \text{ kJ mol}^{-1}}$

w  $w = -P\Delta V = -\Delta nRT = -(1)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(307.5 \text{ K})$   
 $\Delta n = +1$  (1 mole liq. (negligible vol)  $\rightarrow$  1 mole gas (assumed ideal))

$$w = \underline{-2.56 \text{ kJ mol}^{-1}}$$

$\Delta U$   $\Delta U = q + w = 26.0 \text{ kJ mol}^{-1} + (-2.56 \text{ kJ mol}^{-1})$

$\Delta U = \underline{23.4 \text{ kJ mol}^{-1}}$  heat put in to system (+) work done by system on surr (-)

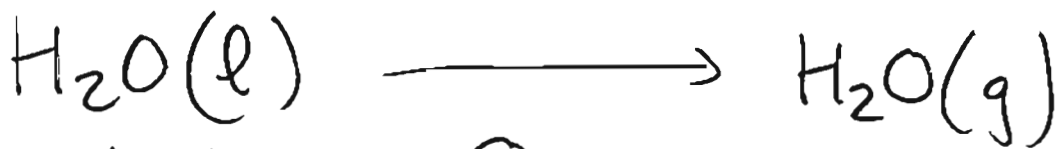
$\Delta S$   $\Delta S^\circ = \frac{q_{\text{rev}}}{T} = \frac{\Delta H^\circ}{T} = \frac{26 \times 10^3 \text{ J mol}^{-1}}{307.5} = \underline{84.6 \text{ J K}^{-1} \text{ mol}^{-1}}$

$\Delta G$  System is at equilibrium (liq. & gas in equilib. at 1 atm)  
 $\Delta G = \Delta G^\circ = 0$

$K = 1 \text{ atm}$  i.e. at equilibrium under std. state conditions.

ADD. PROBS. 6

Consider the system. Given values for  $S^\circ$ ,  $\Delta H_f^\circ$ ,  $\Delta G_f^\circ$



① Is this spont. under std. conditions? at 298 K

② Calc. the vap. press. at 298K.

WATER

③ What is the vap. press of  $H_2O$  at  $50^\circ C$ ?

Think about the  $\Delta G_{rxn}$  and  $\Delta G^\circ$  in these situations. (no solns. provided)

④ At what temp. will the vap. press = 760 torr (1 atm)?