

## Problem set 6 – Chemical Equilibrium and Electrochemistry

### Exercise Maths 6

The Clausius-Clapeyron equation (in integrated form) is given by

$$\ln \frac{p}{p^\ominus} = -\frac{\Delta_{trs}H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right),$$

where  $T_1$  is the transition temperature at  $p^\ominus$  (and thus constant). Rearrange the Clausius-Clapeyron equation to show that in a plot of  $\ln(p/p^\ominus)$  as a function of  $\frac{1}{T_2}$  (hence,  $T_2$  is the ‘running variable’)

- the slope is given by  $-\frac{\Delta_{trs}H}{R}$ ,
- and the intercept is  $\frac{\Delta_{trs}H}{RT_1}$ .

### Exercise 26

For the reaction,  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ , it is found that between 400 and 500 K, the standard reaction Gibbs free energy,  $\Delta_r G^\ominus$  (in  $\text{J mol}^{-1}$ ), varies with the temperature according to

$$\Delta_r G^\ominus = 83680 - 14.52T \ln T - 72.26T.$$

- Calculate  $\Delta_r G^\ominus$ ,  $K_p$ ,  $\Delta_r S^\ominus$  and  $\Delta_r H^\ominus$  for the reaction at 450 K.
- The reaction is started with  $n$  moles of  $\text{PCl}_5$  and at equilibrium, a fraction  $\alpha$  of this amount has dissociated to give a final total pressure of  $p$ . Complete the following table:

	$\text{PCl}_5$	$\text{PCl}_3$	$\text{Cl}_2$	total
no. moles at start	$n$	0	0	
no. moles at equilibrium	$n(1 - \alpha)$			$n(1 + \alpha)$
mole fraction ( $x_i$ )		$\frac{\alpha}{1+\alpha}$		
partial pressure ( $p_i$ )				$p$

- Show that the equilibrium constant can be expressed as

$$K_p = \frac{\alpha^2}{(1 + \alpha)(1 - \alpha)} \frac{p}{p^\ominus}.$$

- Given that the reaction takes place in a container of volume  $V$  and assuming the gases behave as perfect gases, show that  $p$  and, hence,  $K_p$  can be expressed as

$$p = \frac{n(1 + \alpha)RT}{V}, \quad \text{and} \quad K_p = \frac{\alpha^2}{(1 - \alpha)} \frac{nRT}{p^\ominus V}.$$

- Calculate the degree of dissociation  $\alpha$  of  $\text{PCl}_5$  when 0.01 mole of  $\text{PCl}_5$  is introduced into a container of volume  $1 \text{ dm}^3$  at 450 K and allowed to come to equilibrium.

## Exercise 27

- a) Starting from  $\Delta_r G^\ominus = -RT \ln K_p$ , use the Gibbs-Helmholtz equation,  $\left(\frac{\partial(G/T)}{\partial T}\right)_p = -\frac{H}{T^2}$ , to derive the Van 't Hoff equation,

$$\frac{d \ln K_p}{dT} = \frac{\Delta_r H^\ominus}{RT^2},$$

which describes the temperature dependence of  $K_p$ .

- b) Integrate the result of part a) to obtain the Van 't Hoff equation in its integrated form:

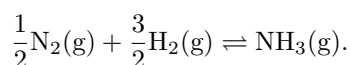
$$\ln \frac{K_2}{K_1} = -\frac{\Delta_r H^\ominus}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right),$$

where  $K_1$  and  $K_2$  are  $K_p$  at  $T_1$  and  $T_2$ , respectively.

- c) For a given reaction, the value of  $K_p$  doubles on changing the temperature from 298 K to 308 K. Calculate  $\Delta_r H^\ominus$  for the reaction.

## Exercise 28

Consider the following reaction



The standard reaction Gibbs energy of  $\text{NH}_3(\text{g})$  is  $-16.49 \text{ kJ mol}^{-1}$  at 298 K and the standard reaction enthalpy is  $-46.11 \text{ kJ mol}^{-1}$ . Assuming that  $\Delta_r H^\ominus$  is independent of temperature, calculate the equilibrium constant,  $K_p$ , for the reaction at

- a) 298 K and 1000 K.

Then find

- c) the temperature at which  $K_p = 1$ ,  
d) **Bonus (extra challenging):** and the amounts of  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  present when 1 mole of  $\text{NH}_3$  is allowed to come to equilibrium at this temperature (where  $K_p = 1$ ) and 1 atm pressure. **Hint:** make a table like in Exercise 26.

## Exercise 29

For the following cell at 25°C:



the standard electrode potentials are  $E_{\text{Sn}/\text{Sn}^{2+}}^\ominus = -0.136\text{V}$  and  $E_{\text{Al}/\text{Al}^{3+}}^\ominus = -1.61\text{V}$ . State or calculate:

- a) the cell reaction and the standard cell potential,  
b) the cell potential when all activities are i) 1 and ii) 0.1,  
c)  $\Delta_r G^\ominus$  and the equilibrium constant for the cell reaction.

## Exercise 30

The following cell,



has a cell potential of 0.559 V at 25°C.

- a) Determine the standard electrode potential for the Cu/CuBr couple.

The solubility product of a salt is defined as the equilibrium constant  $K_s$  for a solid salt dissolving in an aqueous solution. For example, for the reaction  $\text{Ag}_2\text{CO}_3(\text{s}) \rightleftharpoons 2\text{Ag}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$ , the solubility product is given by  $K_s = a_{\text{Ag}^+}^2 a_{\text{CO}_3^{2-}}$ .

Now, the standard hydrogen electrode has been replaced by the Cu/Cu<sup>+</sup> couple, whose standard electrode potential is +0.522 V.

- b) Write down the correct half reactions and the overall cell reaction.  
c) Calculate the solubility product of CuBr(s).

## Exercise 31

The temperature dependence of the standard potential of the cell,



can be expressed in the form (with  $T$  the temperature in K):

$$E_{\text{cell}}^{\ominus}/\text{V} = 0.2366 - 4.856 \times 10^{-4}(T - 273) - 3.421 \times 10^{-6}(T - 273)^2$$

Write down the cell reaction and calculate  $\Delta G^{\ominus}$ ,  $\Delta S^{\ominus}$  and  $\Delta H^{\ominus}$  at 298K.