

## Assignment: Free Energy and Equilibrium Constant

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

The above equation allows us to find the equilibrium constant of a reaction if we know the change in standard free energy and vice versa. The following table summarizes the three possible relations between  $\Delta G^{\circ}$  and  $K$ , as predicted by the above equation ...

$K$	$\ln K$	$\Delta G^{\circ}$	Comments
$> 1$	positive	negative	Products are favoured over reactants at equilibrium
$< 1$	negative	Positive	Reactants are favoured over products at equilibrium
$= 1$	0	0	Products and reactants are equally favoured at equilibrium

Note: when solving the above equation that the unit of  $\Delta G^{\circ}$  is J or kJ and those of  $RT \ln K$  are J/mol, and  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ .

For reactions having very large or very small equilibrium constants, it is generally very difficult to measure the  $K$  values by monitoring the concentrations of all the reacting species. For this reason it is easier to measure the equilibrium constant from  $\Delta G^{\circ}$ .

Since,  $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$ , combining this with the above equation, gives us,

$$\ln K = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$

$\Delta H^{\circ}$  and  $\Delta S^{\circ}$  vary very little with temperature and can be treated as constants over a limited temperature range. A plot of  $\ln K$  against  $1/T$  should therefore be a straight line where the slope =  $-\Delta H^{\circ}/R$ , and the intercept =  $\Delta S^{\circ}/R$ .

We can therefore use a series of measurements of equilibrium constants at different temperatures in two important ways ...

1. We can calculate a value for  $\Delta H^{\circ}$ . This method is often applied when calorimetry cannot be used.
2. We can obtain values of  $K$  for temperatures other than those at which measurements were taken.

It is not always necessary to plot a graph of  $\ln K$  against  $1/T$  in order to estimate  $K$  at some other temperature. We can derive an expression which enables you to calculate  $K$  directly.

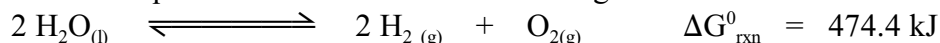
Let  $K_1$  = equilibrium constant at temperature  $T_1$  and  $K_2$  = equilibrium constant at temperature  $T_2$ . Then ...

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

Thus, if four of the quantities  $\Delta H^{\circ}$ ,  $K_1$ ,  $K_2$ ,  $T_1$  and  $T_2$  are known, the fifth may be calculated.

## Problems

1. Calculate the equilibrium constant for the following reaction at 25 °C :

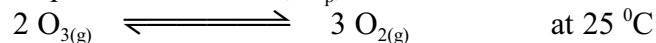


Comment upon the value determined.

$$R = 8.314 \text{ J/K.mol}$$

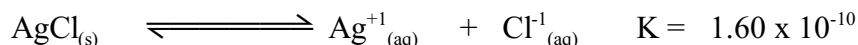
(Ans:  $K_p = 7 \times 10^{-84}$ , consistent with the fact that water does not decompose into hydrogen and oxygen gases at 25 °C)

2. Calculate the equilibrium constant,  $K_p$ , for the reaction :



(Note: first determine  $\Delta G^{\circ}_{\text{rxn}}$  from thermodynamic tables)

3. Calculate  $\Delta G^{\circ}_{\text{rxn}}$  at 25 °C for the following reaction, and comment upon the solubility of  $\text{AgCl}_{(s)}$  :



(Ans:  $\Delta G^{\circ} = 56 \text{ kJ}$ , indicating that  $\text{AgCl}$  is slightly soluble and that the equilibrium lies mostly to the left.)

4. At 1065 °C,  $K_p = 0.0118 \text{ atm}$  for the reaction:



Calculate the equilibrium constant for the reaction at 1200 °C.

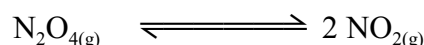
(Ans:  $K_2 = 0.0510 \text{ atm}$ )

5. A particular reaction has a value of  $K_p = 2.44 \text{ atm}$  at 1000 K and 3.74 atm at 1200 K.

Calculate  $\Delta H^{\circ}$  for this reaction.

(Ans:  $\Delta H^{\circ} = 21.3 \text{ kJmol}^{-1}$ )

6. The data below was collected for the reaction:



T (K)	1/T (K <sup>-1</sup> )	K <sub>p</sub> (atm)	ln K <sub>p</sub>
350	2.86 x 10 <sup>-3</sup>	3.89	
400	2.50 x 10 <sup>-3</sup>	4.79 x 10 <sup>1</sup>	
450	2.22 x 10 <sup>-3</sup>	3.47 x 10 <sup>2</sup>	
500	2.00 x 10 <sup>-3</sup>	1.70 x 10 <sup>3</sup>	

a) Determine ln K<sub>p</sub>

b) Plot a graph of ln K<sub>p</sub> (y-axis) against 1/T (x axis)

c) Measure the slope of the graph and so calculate  $\Delta H^{\circ}$  for this reaction. (Ans: 58.3 kJ mol<sup>-1</sup>)

d) What is the value of K<sub>p</sub> at (i) 375 K, (ii) 475 K, (iii) 550 K

What assumption must you make to determine K<sub>p</sub> at 550 K?

e) Use the graph to determine the effect of an increase in temperature on the position of equilibrium for this reaction.