

# Thermodynamics

## Introduction

Teachers who have not used the problems before should read the section Using the problems before starting.

## Prior knowledge

Algebraic definition of pH, and  $K_w$ ; and the relationships between equilibrium constant, standard free energy change, standard enthalpy change, standard entropy change and standard electrode potential. A detailed knowledge is unnecessary as students are encouraged to consult textbooks and data books during the exercise. NB To get the students started, you may have to tell them the value of  $K_w$ , if necessary by explaining that the pH of pure water is 7.

## Resources

Scientific calculators, and perhaps data books for thermodynamic constants should be available. Students are not allowed to use thermodynamic data such as  $E^\ominus$ , so they will have to know the difference between thermodynamic constants and thermodynamic data.

## Group size

3.

## Possible method

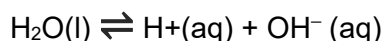
The following can be calculated starting from the pH of water: the dissociation constant of water,  $\Delta G^\ominus$  and  $E^\ominus$ , then using  $\Delta H^\ominus$ ,  $\Delta S^\ominus$ .

1. For pure water, pH = 7 at 25°C

$$[\text{H}^+(\text{aq})] = 10^{-7} \text{ mol dm}^{-3}$$

Since water is neutral,

$$[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})] = 10^{-7} \text{ mol dm}^{-3}$$



$$K = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})] = 1 \times 10^{-14} \text{ (see Background information)}$$

$$\Delta G^\ominus = -RT \ln K$$

$$= -8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times -32.2$$

$$= 79.8 \text{ kJ mol}^{-1},$$

or  $-79.8 \text{ kJ mol}^{-1}$  for the reverse reaction, where  $\Delta H^\ominus$  is given.



$$\Delta G^\ominus = -79.8 \text{ kJ mol}^{-1}$$

$$2. \Delta G^\ominus = -nFE^\ominus$$

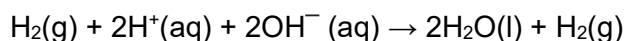
$$E^\ominus = -\Delta G^\ominus/nF = 79800/96500 \text{ V}$$

$$= 0.83 \text{ V}$$

NB Any  $E^\ominus$  is the emf for a galvanic cell. In this case the cell could be constructed from the following two half-reactions:



Overall this gives



$$E^\ominus_{\text{cell}} = 0.83 \text{ V}$$

$$3. \Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

$$T\Delta S^\ominus = \Delta H^\ominus - \Delta G^\ominus = -57.1 - (-79.8) \text{ kJ mol}^{-1}$$

$$= 22.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\ominus = \frac{22700}{298}$$

$$= 76 \text{ J mol}^{-1} \text{ K}^{-1}$$

Because this value is positive the  $\text{H}^+(\text{aq})$  and  $\text{OH}^-(\text{aq})$  must be more ordered than  $\text{H}_2\text{O}(\text{l})$ . This should provoke discussion about the ordering of water molecules round the  $\text{H}^+(\text{aq})$  and the  $\text{OH}^-(\text{aq})$ .

Students may calculate the temperature at which the dissociation of water becomes feasible, ie when  $K \geq 1$ . If so, you could point out that this figure is meaningless because none of the reactants or products can exist at the calculated temperature.

### Suggested approach

During trialling the following instructions were given to students and proved to be extremely effective:

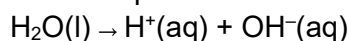
- 1 Working as a group discuss the problem and decide what you can calculate. You should divide the work amongst yourselves but keep one another informed of your progress.  
Such discussion can play a vital part in working out a solution to an open-ended problem like this where divergent thinking is required. Several minds working on a problem together can stimulate ideas that one on its own could not manage. About 10 minutes should be spent on this problem initially with further discussion as required.
- 2 Write a brief account of your findings.
- 3 Working as a group, prepare a short (ca 5-minute maximum) presentation to give to the rest of the class. If possible all group members should take part: any method of presentation (such as a blackboard, overhead projector, etc) can be used.

Outline the problem, describe and explain what you did; do not go through the detailed calculation. If possible try and think back to how you decided on what you could calculate. After the presentation, be prepared to accept and answer questions and to discuss what you did with the rest of the class.

### Possible extension

Once the students have calculated as much as they can, ask them to consider qualitative factors such as the variation of the equilibrium constant with temperature.

For example the dissociation of water:



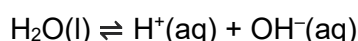
is endothermic, and so the equilibrium constant will increase with increasing temperature. Take  $K_w$  for example

Temperature (°C)	0	10	20	24	30	40	50	60
$pK_w$	14.9	14.5	14.2	14.0	13.8	13.5	13.3	13.0

Therefore, it is only at 24°C that the pH of pure water is exactly seven. It is still neutral at other temperatures, however, because the concentrations of  $H^+(aq)$  and  $OH^-(aq)$  are equal; at 24°C their concentration is  $10^{-7} \text{ mol dm}^{-3}$ , and the pH is 7. (At other temperatures, this is not the case – for example at 0°C the pH of water is 7.5 and at 60°C it is 6.5.)

### Background information

The equation used above is



$$\text{with } K = [H^+(aq)][OH^-(aq)] = 1 \times 10^{-14}$$

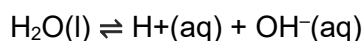
As explained earlier, this expression assumes that the activity of the pure solvent (water) is unity, ie that  $[H_2O(l)]$  is unity. Students who have not met this concept may carry out the calculation as set out below and will get the wrong answer. You should intervene during the discussion to explain the problem and the correct procedure.

However, credit could be given for using the correct equations.

To work out the value of  $[H_2O(l)]$ , students may argue as follows:

18 g of water = 1 mole, so 1000 g = 1000/18 mole

But 1000 g water = 1 dm<sup>3</sup> of water concentration of water = no of moles water in one dm<sup>3</sup>  
= 1000/18



$$[H^+(aq)][OH^-(aq)] = 10^{-14}$$

$$K = \frac{[H^+(aq)][OH^-(aq)]}{[H_2O(l)]} = \frac{10^{-14}}{1000/18} = 1.8 \times 10^{-16} \text{ mol dm}^{-3}$$

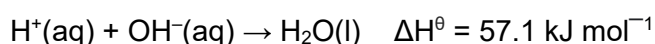
(The reverse of the equation will get the reciprocal of this figure,  $5.6 \times 10^{15} \text{ dm}^3 \text{ mol}^{-1}$ ).

$$\Delta G^\ominus = -RT \ln K = -8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times -36.25$$

$$= 89.8 \text{ kJ mol}^{-1}$$

or  $-89.8 \text{ kJ mol}^{-1}$  for the reverse reaction, for which we have  $\Delta H^\ominus$ .

ie for



$$\Delta G^\ominus = -89.8 \text{ kJ mol}^{-1}$$

$$\Delta G^\ominus = -nFE^\ominus$$

$$E^\ominus = -\Delta G^\ominus/nF = 89800/96500 \text{ V}$$

$$= 0.93 \text{ V (incorrect figure as explained above)}$$

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

$$T\Delta S^\ominus = \Delta H^\ominus - \Delta G^\ominus$$

$$= 32.7 \text{ kJ mol}^{-1}$$

$$\Delta S^\ominus = \frac{32700}{298} = 110 \text{ J mol}^{-1} \text{ K}^{-1}$$

### Notes

1. K is dimensionless. By the derivation of  $\Delta G^\ominus$ , K is a ratio of activities. Hence in this case;

$$K = \frac{\text{activity of H}^+ \times \text{activity of OH}^-}{\text{activity of H}_2\text{O}}$$

The activity of pure liquid is unity, so the activity of water is very close to unity, therefore

$$K = \text{activity of H}^+(\text{aq}) \times \text{activity of OH}^-(\text{aq})$$

Thus  $\Delta G^\ominus$  refers to the reaction when one mole of pure water dissociates to give one mole of  $\text{H}^+$  at unit activity and one mole of  $\text{OH}^-$  at unit activity. For a solute, molality (abbreviation m – moles solute per 1000 g solvent) is generally used. Standard state is the hypothetical ideal state with  $m = 1$ , and at low solute concentrations, activity  $\rightarrow$  molality numerically.

2. A pure number has to be inserted here – the fact that K as used here has units could indicate to the students that there is a problem. By substituting this numerical value for K in the equation for  $\Delta G^\ominus$  we would be considering the process whereby one mole of water at  $1 \text{ mol dm}^{-3}$  concentration is converted to  $1 \text{ mol H}^+$  at  $1 \text{ mol dm}^{-3}$  and  $1 \text{ mol OH}^-$  at  $1 \text{ mol dm}^{-3}$ .

## Thermodynamics

The standard enthalpy of neutralisation (strong acid and strong base) is:



By using this and any other information calculate as many thermodynamic quantities as you can for this reaction.

This problem gives little information, and at first it may appear impossible to solve. However, by discussing the problem, by probing your memory and by referring to textbooks, you should be able to arrive at some answers. Scientific calculators are required.

You should refer to any sources of information that you think might help, such as your notebooks, textbooks and data books. However, you do have to show how you arrived at your answers by calculations rather than getting the answers directly from books. The only numbers you can get from books are values for thermodynamic constants, such as the gas constant.