• In an experiment, NOCl (2.00 mol) was placed in a closed 1.00 L flask. After equilibrium was established at 25 °C, the concentration of NO(g) was 0.66 M. Calculate the value of *K*<sub>c</sub> at 25 °C for the following reaction.

Marks 9

 $2NOCl(g) \iff 2NO(g) + Cl_2(g)$ 

The initial concentration of NOCl is:

 $[NOCl(g)] = \frac{number of moles}{volume} = \frac{(2.00 \text{ mol})}{(1.00 \text{ L})} = 2.00 \text{ M}$ 

The reaction table is:

|             | 2NOCl(g)        | + | 2NO(g) | Cl <sub>2</sub> (g), |
|-------------|-----------------|---|--------|----------------------|
| initial     | 2.00            |   | 0      | 0                    |
| change      | -2 <i>x</i>     |   | +2x    | +x                   |
| equilibrium | 2.00-2 <i>x</i> |   | 2x     | x                    |

As  $[NO(g)]_{equilibrium} = 0.66 \text{ M}, x = 0.33 \text{ M}$  and so:

 $[NOCl(g)] = (2.00 - 2x) M = 1.34 M and [Cl_2(g)]_{equilibrium} = 0.33 M.$ 

The equilibrium constant in terms of concentrations, K<sub>c</sub>, is therefore:

$$K_{\rm c} = \frac{[\rm NO(g)]^2[\rm Cl_2(g)]}{[\rm NOCl(g)]^2} = \frac{(0.66)^2 \times (0.33)}{(1.34)^2} = 0.080$$

 $K_{\rm c} = 0.080$ 

Calculate the value of  $K_p$  at 25 °C for the reaction above.

In the reaction, 2 mol of gas reacts to give (2 + 1) mol = 3 mol of gas.

Hence,  $\Delta n = +1$ .

Using,  $K_{\rm p} = K_{\rm c} (RT)^{\Delta n}$ :

 $K_p = 0.080 \times (0.08206 \times (25 + 273))^1 = 196$ 

 $K_{\rm p} = 196$ 

ANSWER CONTINUES ON THE NEXT PAGE

Given that  $\Delta H_{\rm f}^{\circ}$  for NOCl(g) = 51.71 kJ mol<sup>-1</sup> and  $\Delta H_{\rm f}^{\circ}$  for NO(g) = 90.29 kJ mol<sup>-1</sup> at 25 °C, calculate the value of  $\Delta H^{\circ}$  for the reaction above.

Using 
$$\Delta_{rxn} H^0 = \sum m\Delta_f H^0$$
 (products)  $-\sum n\Delta_f H^0$  (reactants):  
 $\Delta_{rxn} H^0 = [2\Delta_f H^0 (NO(g) + \Delta_f H^0 (Cl_2(g)) - [2\Delta_f H^0 (NOCl(g))]]$   
 $= ([2 \times 90.29 + 0] - [2 \times 51.71] \text{ kJ mol}^{-1}) = 77.16 \text{ kJ mol}^{-1}$   
 $\Delta H^0_{rxn} = +77.16 \text{ kJ mol}^{-1}$ 

What is the effect upon the [NOCl] of an equilibrium mixture if the temperature is increased?

As the reaction is endothermic, the forward reaction becomes more favourable when the temperature is increased. The amount of reactant (NOCl(g)) present at equilibrium therefore decreases.

In which direction will the equilibrium shift if the volume of the flask is reduced?

Reducing the volume of the flash acts to increase the pressure and the system responds to reduce it. The number of moles of gas increases in the reaction so reducing the volume favours reactants and the equilibrium shifts to the left.

• Equal volumes of carbon monoxide and hydrogen gas are introduced into a sealed 4.5 L flask at 1200 K and the following equilibrium is established.

$$CO(g) + 3H_2(g) \iff CH_4(g) + H_2O(g) \qquad \Delta H^\circ = -205.9 \text{ kJ mol}^{-1}$$

At equilibrium, the flask contains 0.22 mol of  $CH_4$  and the total pressure in the flask is 46.4 atm. Calculate the amount of  $H_2(g)$  (in mol) that was initially introduced into the flask.

| erms of moles, the reaction table is: |       |                     |               |                     |                     |  |  |
|---------------------------------------|-------|---------------------|---------------|---------------------|---------------------|--|--|
|                                       | CO(g) | 3H <sub>2</sub> (g) | <del>~`</del> | CH <sub>4</sub> (g) | H <sub>2</sub> O(g) |  |  |
| initial                               | x     | <u>X</u>            |               | 0                   | 0                   |  |  |
| change                                | -y    | -3y                 |               | + <i>y</i>          | + <i>y</i>          |  |  |
| equilibrium                           | x - y | x-3y                |               | у                   | у                   |  |  |

(Three  $H_2$  molecules are lost for every one CO molecule and hence the change in the number of moles of CO(g) and  $H_2(g)$  are -y and -3y respectively).

As 0.22 mol of  $CH_4(g)$  is present at equilibrium, y = 0.22 mol.

The total number of moles present is therefore:

total number of moles = 
$$n_{CO(g)} + n_{H_2(g)} + n_{CH_4(g)} + n_{H_2O(g)}$$
  
=  $(x - y) + (x - 3y) + (y) + (y) = 2x - 2y = 2x - 0.44$  mol

As the pressure in the flask is 46.4 atm at equilibrium, the number of moles of gas at equilibrium is can be calculated from the ideal gas law, PV = nRT:

$$n = \frac{PV}{RT} = \frac{(46.4 \text{ atm}) \times (4.5 \text{ L})}{(0.08206 \text{ L atm } \text{ K}^{-1} \text{ mol}^{-1}) \times (1200 \text{ K})} = 2.12 \text{ mol}$$

Hence, 2x - 0.44 = 2.12 and x = 1.28 mol = initial number of moles of H<sub>2</sub>(g)

Answer: 1.28 mol

In a separate experiment, it is determined that the reaction is in equilibrium when the same 4.5 L flask contains 0.18 mol of  $CH_4$ , 0.24 mol of  $H_2O$ , 0.82 mol of CO and 0.65 mol of  $H_2$  at 1200 K. Calculate the concentration equilibrium constant,  $K_c$ , for this temperature.

$$[CH_4(g)] = \frac{0.18 \text{ mol}}{4.5 \text{ L}} = 0.040 \text{ M}, [H_2O(g)] = \frac{0.24 \text{ mol}}{4.5 \text{ L}} = 0.053 \text{ M}$$
$$[CO(g)] = \frac{0.82 \text{ mol}}{4.5 \text{ L}} = 0.18 \text{ M}, [H_2(g)] = \frac{0.65 \text{ mol}}{4.5 \text{ L}} = 0.14 \text{ M}$$
$$Hence, K_c = \frac{[CH_4(g)][H_2O(g)]}{[CO(g)][H_2(g)]^3} = \frac{(0.040) \times (0.53)}{(0.18) \times (0.14)^3} = 3.9$$
$$K_c = 3.9$$

Marks 5 CHEM1909

## 2004-N-5

| Calculate the partial pressure equilibrium constant, $K_p$ , at 1200 K.   |   |  |  |  |  |
|---|---|--|--|--|--|
| In the reaction CO(g) + $3H_2(g) \iff CH_4(g) + H_2O(g)$ , 4 moles of gas react to form 2 moles of gas – a <i>decrease</i> of 2 moles of gas or $\Delta n = -2$ mol.              |   |  |  |  |  |
| From the previous question (2004-N-4), $K_c = 3.9$ . As $K_p$ and $K_c$ are related by $K_p = K_c (RT)^{\Delta n}$  |   |  |  |  |  |
| $K_p = 3.9 \times (0.08206 \times 1200)^{-2} = 4.0 \times 10^{-4}$  |   |  |  |  |  |
| $K_{\rm p} = 4.0 \times 10^{-4}$  |   |  |  |  |  |
| What is the standard free energy change $\Delta G^{\circ}$ for the forward reaction (in kJ mol <sup>-1</sup> ) at 1200 K?   |   |  |  |  |  |
| Using $\Delta G^{\circ} = -RT \ln K_{\rm p}$ :  |   |  |  |  |  |
| $\Delta G^{\circ} = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1200 \text{ K}) \times \ln(4.0 \times 10^{-4})$<br>= -78000 J mol <sup>-1</sup> = -78 kJ mol <sup>-1</sup> |   |  |  |  |  |
| $\Delta G^{\circ} = -78 \text{ kJ mol}^{-1}$  |   |  |  |  |  |
| What will be the effect on the equilibrium if CO(g) is injected into the flask, which maintains a constant volume.  |   |  |  |  |  |
|   | 1 |  |  |  |  |

The equilibrium will shift to reduce the amount of CO(g). It will shift towards products.

What will be the effect on the equilibrium if the temperature is decreased?

The reaction is exothermic (see previous question (2004-N-4)) so the reaction will shift to give out more heat. It will shift towards products.

What will be the effect on the equilibrium if the volume of the flask is decreased?

If the volume is decreased, the pressure will increase. The reaction will shift to reduce the pressure. As the forward reaction leads to a decrease in the amount of gas, the equilibrium will shift towards products.

What will be the effect on the equilibrium if the walls of the flask are refrigerated so that liquid water condenses out?

If  $H_2O(g)$  is removed to form pure  $H_2O(l)$ , the equilibrium will shift to increase the concentration of H<sub>2</sub>O(g). The equilibrium will shift towards products.

Marks

| Equimolar amoun<br>Vhen the system<br>lask is 4.04 × 10 <sup>-</sup><br>lask?                                      | ts of NOCl(g) a<br>reaches equilibr<br><sup>4</sup> M. What amo  | and $Cl_2(g)$ are intro-<br>rium at 35 °C, the open of $Cl_2(g)$ (in r                     | oduced into a seconcentration of nol) was initial  | ealed 1.00 L flask.<br>of NO(g) in the<br>ly added to the                        |
|--|--|--|--|--|
| If the initial con<br>reaction table is  | centrations of (<br>:  | Cl <sub>2</sub> (g) and NOCl   | (g) are both e   | qual to <i>x</i> , the   |
|  | <b>Cl</b> <sub>2</sub> ( <b>g</b> )  | 2NO(g)   | +  | 2NOCl(g)   |
| initial  | x  | 0  |  | x  |
| change   | +y   | +2 <i>y</i>  |  | -2 <i>y</i>  |
| equilibrium  | x + y  | 2y   |  | x-2y   |
| As [NO(g)] <sub>equilibr</sub><br>[Cl <sub>2</sub> (g)] <sub>equilibr</sub><br>[NOCl(g)] <sub>equ</sub>            | $u_{ium} = 2y = 4.04$ $u_{ium} = x + y$              | × $10^{-4}$ M, $y = 2.02$<br>+ $2.02 \times 10^{-4}$ M and $x = x - 4.04 \times 10^{-4}$ M | 2 × 10 <sup>-4</sup> M and<br>nd<br>1  | so:  |
| From the equilil   | orium constant   | :  |  |  |
| $K_{\rm c} = \frac{[\rm NO]}{[\rm Cl_2(g)]}$   | $\frac{\left \operatorname{Cl}(\mathbf{g})\right ^{2}}{\left \left[\operatorname{NO}(\mathbf{g})\right]^{2}\right } = \frac{1}{\left(\frac{1}{2}\right)^{2}}$  | $\frac{(x-4.04 \mathrm{x} 10)}{(x+2.02 \mathrm{x} 10^{-4})(4.00)}$                         | $(\frac{-4}{2})^2$<br>$(\frac{1}{2})^2$  |  |
| As the equilibriu<br>amount of Cl <sub>2</sub> a   | ım for the <i>forw</i><br>nd NO that are<br>assumed that t   | <i>ward</i> reaction is ve<br>produced in the<br>his amount (4.04                          | ery large (6.25<br><i>backward</i> rea<br>x 10 <sup>-4</sup> ) is smal                       | x 10 <sup>4</sup> ), the<br>ction is very<br>l compared to x.                    |
| small. It can be   | x 10 <sup>-4</sup> ~ x and x   | $x - 4.04 \times 10^{-4} \sim x$ :   |  |  |
| small. It can be<br>Hence, x + 2.02  |  |  | $r^2$  |  |
| small. It can be a<br>Hence, $x + 2.02$ a<br>$K_c = \frac{1}{(x+2)}$   | $\frac{(x-4.04 \times 10^{-4})}{.02 \times 10^{-4}}$   | $\frac{x^2}{x^{10^{-4}}} \sim \frac{x}{x^{(4.04)}}$  | $\frac{x}{x10^{-4}}^2 = \frac{x}{(4.0)^2}$   | $\frac{x}{(10^{-4})^2}$  |
| small. It can be a<br>Hence, $x + 2.02$ and $K_c = \frac{1}{(x+2)}$<br>As $K_c = 6.25 \times 1$<br>L, the number o | $\frac{(x-4.04 \times 10^{-4})}{.02 \times 10^{-4}}$ $(4.04)$ $(10^{-4})$ $(10^$ | $(x^{2})^{2} = x = 0.0102$ M. A<br>entration × volume                                      | $\frac{1}{x + 10^{-4}} = \frac{1}{(4.0)^{4}}$<br>As the volume<br>$x = 0.0102 \times 10^{4}$ | $\frac{x}{(14 \times 10^{-4})^2}$<br>e of the flask is 1.00<br>1.00 = 0.0102 mol |

At the same temperature (35 °C) O<sub>2</sub>(g) reacts with NO(g) according to the equation:

$$O_2(g) + 2NO(g) \iff 2NO_2(g)$$
  $K_c = 6.25 \text{ M}^{-1}$ 

Determine  $K_c$  for the following reaction.

 $2NO_2(g) + Cl_2(g) \implies 2NOCl(g) + O_2(g)$ 

The equilibrium constants for the three reactions are:

$$K_{c}(1) = \frac{[\text{NOCl}]^{2}}{[\text{Cl}_{2}][\text{NO}]^{2}}, K_{c}(2) = \frac{[\text{NO}_{2}]^{2}}{[\text{O}_{2}][\text{NO}]^{2}} \text{ and } K_{c}(3) = \frac{[\text{NOCl}]^{2}[\text{O}_{2}]}{[\text{NO}_{2}]^{2}[\text{Cl}_{2}]}$$

so that

$$\frac{K_{\rm c}(1)}{K_{\rm c}(2)} = \frac{[\rm NOCI]^2}{[\rm Cl_2][\rm NO]^2} / \frac{[\rm NO_2]^2}{[\rm O_2][\rm NO]^2} = \frac{[\rm NOCI]^2[\rm O_2]}{[\rm NO_2]^2[\rm Cl_2]} = K_{\rm c}(3)$$

Hence,  $K_{\rm c}(3) = \frac{6.25 \times 10^4}{6.25} = 1.00 \times 10^4$ .

 $K_{\rm c} = 1.00 \times 10^{-4} {\rm M}$ 

Calculate the partial pressure equilibrium constant,  $K_p$ , at 35 °C for the reaction:

$$2NO_2(g) + Cl_2(g) \implies 2NOCl(g) + O_2(g)$$

In the reaction, 3 moles of gas react to form 3 moles of gas – there is no change in the number of moles of gas and so  $\Delta n = 0$ .  $K_c$  was calculated in the previous question (2005-N-5) to be  $1.00 \times 10^{-4}$ 

$$K_{\rm p} = K_{\rm c} (RT)^{\Delta n}$$
  
=  $K_{\rm c} (RT)^0 = K_{\rm c} = 1.00 \times 10^4$ 

 $K_{\rm p} = 1.00 \times 10^{-4}$ 

What is the standard free energy change,  $\Delta G^{\circ}$ , for the forward reaction (in kJ mol<sup>-1</sup>) at 35 °C?

Using  $\Delta G^{\circ} = -RT \ln K_{\rm p}$ ,  $\Delta G^{\circ} = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times ((35 + 273) \text{ K}) \times \ln(1.00 \times 10^{-4})$  $= -23600 \text{ J mol}^{-1} = -23.6 \text{ kJ mol}^{-1}$ 

 $\Delta G^{\circ} = -23.6 \text{ kJ mol}^{-1}$ 

If 0.150 mol of  $O_2(g)$  and  $3.00 \times 10^{-4}$  mol of  $NO_2(g)$  are added to the 1.00 L flask, determine the free energy change,  $\Delta G$ , (in kJ mol<sup>-1</sup>) as the system moves to its new equilibrium point.

From the previous question (2005-N-5), the initial concentrations of [NOCl] and [Cl<sub>2</sub>] are both equal to 0.0102 M. The concentrations of  $O_2(g)$  and  $NO_2(g)$  are equal to 0.150 M and  $3.00 \times 10^{-4}$  M as the flask has a volume of 1.00 L.

The reaction quotient, Q, for this reaction is  $Q = \frac{[\text{NOCl}(g)]^2[O_2(g)]}{[\text{NO}_2(g)]^2[\text{Cl}_2(g)]}$ . Hence:

 $Q = \frac{(0.0102)^2(0.150)}{(3.00 \times 10^4)^2(0.0102)} = 17000$  and

 $\Delta G = \Delta G^{\circ} + RT \ln Q = (-23.6 \times 10^{3} \text{ J mol}^{-1}) + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times ((35+273) \text{ K}) \times \ln(17000)$  $= +1.4 \text{ kJ mol}^{-1}$ 

 $\Delta G = +1.4 \text{ kJ mol}^{-1}$ 

Will the amount of  $NO_2(g)$  in the flask increase or decrease as the system moves to its new equilibrium position? Explain.

As  $Q > K_c$ , the system will move to decrease Q. This occurs by reducing the concentration of the products and increasing the concentration of reactants. [NO<sub>2</sub>(g)] will thus increase.

Marks 7 2006-N-6

| The gas s<br>At 9<br>900 This<br>equil<br>conc<br>The | CO(g) in water<br>hift" reaction:<br>00 K, $K_c = 1.56$<br>K contains a 1:<br>sample is place<br>librium, at which<br>entration of CO<br>reaction table | gas can be r<br>CO(g) + H<br>o for this reac<br>1 mole ratio<br>ed in a sealed<br>ch point it co<br>$D(g)$ and $H_2(g)$<br>is | eacted further with $H_2O(g) \iff 0$<br>etion. A sample of $O(g)$ and $H_2(g)$<br>container at 900<br>ntains 0.070 mol<br>g) in the sample?   | th H <sub>2</sub> O(g<br>CO <sub>2</sub> (g) +<br>of water g<br>(g), as we<br>K and a<br>$L^{-1}$ CO <sub>2</sub> | g) in the so-c<br>- $H_2(g)$<br>gas flowing of<br>ell as 0.250 r<br>llowed to co<br>(g). What w | alled "water-<br>over coal at<br>nol $L^{-1} H_2O(g$<br>me to<br>ras the initial | J). |
|---|---|---|---|---|---|--|-----|
|   |   | CO(g)   | H <sub>2</sub> O(g)   | <u> </u>  | CO <sub>2</sub> (g)   | $H_2(g)$   |     |
|   | initial   | X   | 0.250   |   | 0   | X  |     |
|   | change  | -0.070  | -0.070  |   | +0.070  | +0.070   |     |
|   | equilibrium   | x - 0.070   | 0.250 - 0.070   |   | 0.070   | x + 0.070  |     |
| The   | equilibrium co<br>$K_{c} = \frac{[CO_{2}(g)]}{[H_{2}O(g)]}$ $x = [CO(g)]_{tractical}$   | $\frac{\left[\left[H_{2}(g)\right]\right]}{\left[\left[CO(g)\right]\right]} = \frac{0}{0}$                                    | erms of concentration<br>(0.070)(x + 0.070)(x + 0.070)(0.180)(x - 0.070)<br>(0.180)(x - 0.070)(x - | ations, H<br>)<br>) = 1.56  | ζ <sub>c</sub> , is:  |  |     |
| ·   | x – [CO(g)]initi  |   |   | []]] _ <b>(</b> ]   | 12 mal I -1   |  |     |
|   |   |   | [[CO] =   | $[H_2] = 0$   | $12 \text{ mol } L^{-1}$  |  |     |
| If the conc   | e walls of the c<br>entration of CC   | ontainer are $O_2(g)$ ?   | chilled to below 1  | 100 °C, v   | what will be t  | he effect on t   | he  |

At temperatures below 100 °C, the water vapour will condense to form  $H_2O(l)$ . Following Le Chatelier's principle, the equilibrium will shift to the left as  $[H_2O(g)]$  is reduced by this process and so  $[CO_2(g)]$  will decrease.

6

Marks The isomerisation of glucose-6-phosphate (G6P) to fructose-6-phosphate (F6P) is a key step in the metabolism of glucose for energy. At 298 K,

> G6P <del>←</del> F6P  $\Delta G^{\circ} = 1.67 \text{ kJ mol}^{-1}$

Calculate the equilibrium constant for this process at 298 K.

Using  $\Delta G^{\circ} = -RTlnK$ ,

 $1.67 \times 10^3 = -(8.314) \times (298) \times \ln K$ 

K = 0.510

Answer: **K** = **0.510** 

What is the free energy change (in kJ mol<sup>-1</sup>) involved in a mixture of 3.00 mol of F6P and 2.00 mol of G6P reaching equilibrium at 298 K?

The reaction quotient, for the reaction, is  $Q = \frac{[F6P]}{[G6P]} = \frac{3.00}{2.00} = 1.50$ .

Using  $\Delta G = \Delta G^{\circ} + RT \ln Q$ ,

 $\Delta G = (1.67 \times 10^3) + (8.314 \times 298) \times \ln(1.50) = +2670 \text{ J mol}^{-1} = +2.67 \text{ kJ mol}^{-1}$ 

Answer: +2.67 kJ mol<sup>-1</sup>

Sketch a graph of  $G_{sys}$  versus "extent of reaction", with a curve showing how  $G_{sys}$ varies as G6P is converted to F6P. Indicate the position on this curve corresponding to 3.00 mol of F6P and 2.00 mol of G6P.



2007-N-3

• Acetylene, C<sub>2</sub>H<sub>2</sub>, can be produced by reacting calcium carbide, CaC<sub>2</sub>, with water:

$$CaC_2(s) \ + \ 2H_2O(l) \ \rightarrow \ Ca(OH)_2(s) \ + \ C_2H_2(g)$$

A 1.000 g sample of CaC<sub>2</sub> is placed in a sealed vessel that contains 250.0 mL of  $H_2O(1)$  and 250.0 mL of  $N_2(g)$  at 1.000 atm, and allowed to react completely with the water. The final pressure in the sealed vessel at 22.0 °C is 2.537 atm. Determine the vapour pressure of water in the sealed vessel at 22.0 °C. Give your answer in mmHg. Ignore any change in the volume of the water.

The formula mass of CaC<sub>2</sub> is (40.08 (Ca) + 2 × 12.01 (C)) g mol<sup>-1</sup> = 64.1 g mol<sup>-1</sup>. The amount of CaC<sub>2</sub> in 1.000 g is therefore,  $n = \frac{m}{M} = \frac{1.000}{64.1} = 0.01560$  mol.

From the chemical equation, each mole of CaC<sub>2</sub> that reacts leads to one mole of C<sub>2</sub>H<sub>2</sub>(g). Therefore, 0.0156 mol of C<sub>2</sub>H<sub>2</sub>(g) is formed. The volume available to gas is 250.0 mL. Using the ideal gas equation, pV = nRT, the pressure due to this amount is therefore:

$$p_{C_2H_2} = \frac{nRT}{V} = \frac{(0.01560 \text{ mol}) \times (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (22 + 273) \text{K}}{0.250 \text{ L}}$$
  
= 1.511 atm

As there is no change in the amount of N<sub>2</sub>(g),  $p_{N_2} = 1.000$  atm. Hence,

$$p_{\text{total}} = p_{\text{H}_2\text{O}} + p_{\text{C}_2\text{H}_2} + p_{\text{N}_2} = 2.537 \text{ atm}$$
  
 $p_{\text{H}_2\text{O}} + (1.511 \text{ atm}) + (1.000 \text{ atm}) = 2.537 \text{ atm}$ 

Hence,  $p_{H_2O} = 0.026$  atm. As 1 atm = 760 mmHg, this corresponds to.

$$p_{\rm H_{2}O} = 0.026 \times 760 = 20 \; \rm mmHg$$

Answer: 20 mmHg

The solubility of acetylene in water at 22.0 °C is small. If the temperature were raised, would you expect this solubility to increase or decrease?

The solubility of gases in water decreases with temperature. The dissolution of a gas is entropically disfavoured and only occurs because it is exothermic. Like all exothermic process, the process becomes less favourable at higher temperatures (Le Chatelier's principle).

Marks • Consider the reaction  $2SO_2(g) + O_2(g) \Longrightarrow$  $2SO_3(g)$ 5  $\Delta H^{\circ} = -198.4 \text{ kJ mol}^{-1} \text{ and } \Delta S^{\circ} = -187.9 \text{ J K}^{-1} \text{ mol}^{-1} \text{ at } 25 \text{ }^{\circ}\text{C}.$ Show that this reaction is spontaneous at 25 °C. For a reaction to be spontaneous,  $\Delta G^{\circ}$  must be negative. As  $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ At T = 25 °C.  $\Delta G^{\circ} = (-198.4 \times 10^3) - (25 + 273) \times (-187.9)$  J mol<sup>-1</sup> = -140 kJ mol<sup>-1</sup> As  $\Delta G^{\circ}$  is negative at this temperature, the reaction is spontaneous. If the volume of the reaction system is increased at 25 °C, in which direction will the reaction move? The reaction involves 3 moles of gas being converted into 2 moles of gas. If the volume is increased, the pressure will decrease and the reaction will therefore shift to increase the number of moles of gas (Le Chatelier's principle). It will shift to the left. Calculate the value of the equilibrium constant, K, at 25 °C. As  $\Delta G^{\circ} = -RT \ln K$ , the equilibrium constant, *K*, at T = 25° is given by  $-140 \times 10^{3} = -8.314 \times (25 + 273) \times \ln K$  or  $K = e^{57}$  $K = 9.2 \times 10^{24}$  $K = 9.2 \times 10^{24}$  (*K* has no units) Assuming  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  are independent of temperature, in which temperature range is the reaction non-spontaneous? The reaction is non-spontaneous when  $\Delta G^{\circ} > 0$ . Assuming  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  are independent of temperature, this will occur when  $\Delta H^{\circ}$  -T $\Delta S^{\circ} > 0$ :  $(-198.4 \times 10^3) - T \times (-187.9) > 0$  $T > \frac{198.4 \times 10^3}{187.9}$  or T > 1056 K

Answer: **T** > **1056 K** 

| • The first step in the metabolism of glucose in biological systems is the addition of a phosphate group in a dehydration-condensation reaction: |  |   |  |  |  |  |  |  |
|--|--|---|--|--|--|--|--|--|
| glucose(aq) + $H_2PO_4^{-}(aq) \iff [glucose phosphate]^{-}(aq) + H_2O(l)$   |  |   |  |  |  |  |  |  |
|  | The free energy reaction is d hydrolysis o                   | ergy change ass<br>riven forwards<br>of adenosine trip<br>$+ H_2O(1) =$ | ociated with th<br>by harnessing<br>bhosphate, ATF<br>$\rightarrow$ ADP <sup>3-</sup> (aq) | is react<br>the free<br>$P^{4-}$ , to a<br>+ HaP | fon is $\Delta G^{\circ} = 13.8$ kJ m<br>energy associated with<br>denosine diphosphate,   | $ol^{-1}$ . The<br>the<br>$ADP^{3-}$ :<br>$30.5 \text{ kL mol}^{-1}$ |  |  |
|  | The overall  | reaction is thus  |  | 1 11/1   | $\Box_4$ (aq) $\Box \Box =$  | 50.5 KJ 1101   |  |  |
|  |  |   | ·<br>-/ ` ` ` `  | 1  |  | $-D^{3-}$  |  |  |
|  | glucos<br>Calculate th<br>temperature                        | $e(aq) + ATP^{*}$<br>e equilibrium c<br>(37 °C).                        | (aq) $-$ [<br>onstant associa  | glucose<br>ted with                              | phosphate] $(aq) + All a constant cons$ | DP <sup>e</sup> (aq)<br>t body                                       |  |  |
|  | The overal<br>glucose(aq                                     | ll reaction is th<br>) + $H_2PO_4^{-}(aq)$                              | e sum of the t   | wo read  | ctions:<br>ΔG<br>sphate] <sup>-</sup> (aq) + H <sub>2</sub> O(l)   | <sup>co</sup> (kJ mol <sup>-1</sup> )<br>13.8                        |  |  |
|  | ATP <sup>4–</sup> (aq)                                       | $+ H_2O(l) $  | = $ADP^{3-}(aq)$ -   | + H <sub>2</sub> PO                              | 4 <sup>-</sup> (aq)  | -30.5  |  |  |
| -  | glucose(aq   | $)+ATP^{4-}(aq)$  | ← [glucose   | phosp  | hate] <sup>-</sup> (aq)+ADP <sup>3-</sup> (aq)   | -16.7  |  |  |
|  | For the ov<br>$\Delta G^\circ = -RT$<br>-16.7                | erall reaction,<br>ln <i>K</i> ,<br>× 10 <sup>3</sup> = -8.314          | $\Delta G^{\circ} = ((13.8) \times (37 + 273) \ln 3)$                                      | + (-30.<br>K or                                  | 5)) kJ mol <sup>-1</sup> = -16.7 kJ<br>K = e <sup>6.48</sup> = 652   | <b>mol<sup>-1</sup>. Using</b>                                       |  |  |
|  |  |   |  | Answe  | r: $K = 652$ (no units)  |  |  |  |
|  | This overall<br>flask contain<br>percentage o<br>equilibrium | equilibrium rea<br>ning 175 mL of<br>of the ATP <sup>4-</sup> wi<br>?   | action is invest<br>a 0.0500 M aq<br>11 have been co                                       | igated b<br>Jueous s<br>Disumed                  | y adding 0.0100 mol o<br>olution of glucose at 3'<br>l when the system reac  | f ATP <sup>4–</sup> to a<br>7 °C. What<br>hes                        |  |  |
|  | The initial<br>table is the                                  | concentration<br>en:  | of ATP <sup>4-</sup> is $\frac{n}{V}$  | $\frac{u}{r}=\frac{0.0}{0}$                      | $\frac{100\text{mol}}{.175\text{L}} = 0.0571\text{M}.$   | The reaction   |  |  |
|  |  | glucose(aq)   | ATP <sup>4-</sup> (aq)   | -  | [glucose<br>phosphate] <sup>-</sup> (aq)   | ADP <sup>3-</sup> (aq)   |  |  |
|  | initial  | 0.0500  | 0.0571   |  | 0  | 0  |  |  |
|  | change   | -X  | -X   |  | +x   | + <b>x</b>   |  |  |
| e  | equilibrium  | 0.0500-x  | 0.05/1-x   |  | X  | X  |  |  |
|  | At equilibing $K = \frac{[g]}{[g]}$                          | rium,<br>u cos e - phospl<br>[glu cos e(a                               | nate <sup>-</sup> (aq)][AD<br>1q)][ATP <sup>4-</sup> (aq                                   | P <sup>3-</sup> (aq<br> )]                       | $\frac{x^2}{(0.0500 - x)(0.057)}$  | $\overline{(1-x)} = 652$   |  |  |
|  | $K = \frac{[\mathbf{gl}]}{\mathbf{gl}}$                      | u cos e - phospl<br>[glu cos e(a  | nate <sup>-</sup> (aq)][AD<br>nq)][ATP <sup>4-</sup> (aq                                   | P <sup>5-</sup> (aq<br>[)]                       | $\frac{x^2}{(0.0500 - x)(0.057)}$  | $\overline{(1-x)} = 652$   |  |  |

As the equilibrium constant is large so is x and this expression cannot be approximated. Instead, the full quadratic equation must be solved.

 $x^2 = 652(0.0500-x)(0.0571-x)$  or

 $651x^2 - 652(0.0500 + 0.0571) + (652 \times 0.0500 \times 0.0571) = 0$ 

The two roots are  $x_1 = 0.0578$  M and  $x_2 = 0.0495$  M. As  $x_1$  gives a negative [glucose(aq)], it is not physically significant. As x is the concentration consumed, using  $x_2$  gives:

percentage of ATP<sup>4-</sup>(aq) consumed =  $\frac{0.0495 \text{ M}}{0.0571 \text{ M}} \times 100\% = 87\%$ 

Answer: **87%** 

Suggest two simple ways of further reducing the remaining percentage of ATP<sup>4-</sup>.

The remaining ATP<sup>4-</sup> can be reduced by (i) adding more glucose and (ii) reducing the temperature. Removal of either product would also drive the reaction to the right but would be very difficult to achieve in practice.

49.0

 $K_{\rm c}(2) = 1/(1.075 \times 10^8)$ 

• At 700 °C, hydrogen and iodine react according to the following equation.

$$H_2(g) + I_2(g) \iff 2HI(g) \qquad K_c =$$

Hydrogen also reacts with sulfur at 700 °C:

 $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ 

$$2H_2(g) + S_2(g) \implies 2H_2S(g) \qquad K_c = 1.075 \times 10^8$$

Determine  $K_c$  for the following overall equilibrium reaction at 700 °C.

$$2I_2(g) + 2H_2S(g) \iff S_2(g) + 4HI(g)$$

The overall reaction corresponds to the twice the first reaction combined with the reverse of the second reaction:

$$2H_2(g) + 2I_2(g) \iff 4HI(g)$$
  $K_c(1) = (49.0)^2$ 

 $2I_2(g) + 2H_2S(g) \implies S_2(g) + 4HI(g)$   $K_c(3) = K_c(1) \times K_c(2)$ 

The 1<sup>st</sup> reaction is doubled so the original equilibrium constant is squared.

The 2<sup>nd</sup> reaction is reversed so the reciprocal of the equilibrium constant is used.

The two reactions are then combined and the overall equilibrium constant is then the product:

$$K_{\rm c}(3) = K_{\rm c}(1) \times K_{\rm c}(2) = (49.0)^2 \times (1/(1.075 \times 10^8) = 2.23 \times 10^{-5})$$

$$K_{\rm c} = 2.23 \times 10^{-5}$$

What is the standard free energy change at 700  $^{\circ}$ C for this overall equilibrium reaction?

The equilibrium constant in terms of pressures is first converted into the equilibrium constant in terms of pressures using  $K_p = K_c(RT)^{\Delta n}$ . The reaction involves the conversion of 4 mol of gas to 5 mol of gas so  $\Delta n = +1$  and:

 $K_{\rm p} = K_{\rm c}(RT)^{\Delta n} = (2.23 \times 10^{-5}) \times (0.08206 \times 973)^1 = 0.00178$ 

Note that as  $K_c$  is in terms of concentration units of mol L<sup>-1</sup>, R = 0.08206 atm L mol<sup>-1</sup> K<sup>-1</sup> has been used.

As  $\Delta G^{\circ} = -RT \ln K_p$ :

 $\Delta G^{\circ} = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})^{\circ} (973 \text{ K}) \times \ln(0.00178) = +51.2 \text{ kJ mol}^{-1}$ 

Answer:  $+51.2 \text{ kJ mol}^{-1}$ 

THIS QUESTION CONTINUES ON THE NEXT PAGE.

If 0.250 mol of HI(g) is introduced into a 2.00 L flask at 700 °C, what will be the concentration of  $I_2(g)$  at equilibrium?

The initial concentration of HI(g) is  $0.250 / 2.00 \text{ mol } \text{L}^{-1} = 0.125 \text{ mol } \text{L}^{-1}$ .

|             | <b>H</b> <sub>2</sub> ( <b>g</b> ) | <b>I</b> <sub>2</sub> ( <b>g</b> ) | <del>~`</del> | 2HI(g)     |
|-------------|------------------------------------|------------------------------------|---------------|------------|
| Initial     | 0                                  | 0                                  |               | 0.125      |
| Change      | +x                                 | +x                                 |               | -2x        |
| Equilibrium | x                                  | x                                  |               | 0.125 - 2x |

Thus,

$$K_{\rm c} = \frac{[{\rm HI}]^2}{[{\rm H}_2][{\rm I}_2]} = \frac{(0.125 - 2x)^2}{(x)(x)} = \frac{(0.125 - 2x)^2}{x^2} = 49.0 \text{ (from 2008-N-5)}$$

$$(49.0)^{1/2} = \frac{(0.125 - 2x)}{x}$$

Rearranging gives  $x = [I_2(g)] = 0.0139$  M.

Answer: 0.0139 M

If 0.274 g of  $H_2S$  were now introduced into the same flask, what would be the concentration of  $S_2(g)$  at equilibrium?

The molar mass of  $H_2S$  is  $(2 \times 1.008 \text{ (H)} + 32.06 \text{ (S)}) = 34.08 \text{ g mol}^{-1}$ . Hence, 0.274 g of  $H_2S$  corresponds to:

number of moles = mass / molar mass =  $(0.274 \text{ g}) / (34.08 \text{ g mol}^{-1}) = 8.04 \times 10^{-3} \text{ mol}$ 

The initial concentration of H<sub>2</sub>S is thus  $8.04 \times 10^{-3}$  mol / 2.00 M =  $4.02 \times 10^{-3}$  M.

From above,  $[I_2(g)] = 0.0139$  M and  $[HI(g)] = (0.125 - 2 \times 0.0139)$  M = 0.00972 M.

Using the overall equilibrium reaction derived in 2008-N-5:

|             | $2I_2(g)$   | 2H <sub>2</sub> S(g) | + | <b>S</b> <sub>2</sub> ( <b>g</b> ) | <b>4HI(g)</b> |
|-------------|-------------|----------------------|---|------------------------------------|---------------|
| Initial     | 0.0139      | 0.00402              |   | 0                                  | 0.00972       |
| Change      | -2x         | -2x                  |   | +x                                 | +2x           |
| Equilibrium | 0.0139 - 2x | 0.00402 - 2x         |   | x                                  | 0.00972 + 4x  |

# ANSWER CONTINUES ON THE NEXT PAGE

Thus,

$$K_{\rm c} = \frac{[S_2][HI]^4}{[I_2]^2[I_2]^2} = \frac{(x)(0.00972 + 4x)^4}{(0.0139 - 2x)^2(0.00402 - 2x)^2}$$
  

$$\sim \frac{(x)(0.00972)^4}{(0.0139)^2(0.00402)^2} = 2.23 \times 10^{-5} \text{ (from 2008-N-5)}$$
  
here the small x approximation has been used as  $K_{\rm c}$  is so small. This gives:

wh

 $x = [S_2(g)] = 7.82 \times 10^{-10} \text{ M}$ 

Answer:  $7.82 \times 10^{-10}$  M

• Explain the meanings of the following terms.

#### Heat

Heat: energy contained in kinetic energies of molecules that flows from hotter to cooler temperatures.

### $P\Delta V$ work

 $P \Delta V$  work: work done by or on a system by a change in volume against a constant pressure.

#### Internal energy

Internal energy: the total energy contained within a system; the difference in internal energy in a system is the sum of the heat and work done by or on the system.

Enthalpy change

Enthalpy change: the difference in enthalpy between an initial and final state, the enthalpy being the heat of a system at constant pressure.

Entropy

Entropy: a measure of the distribution of heat, related to the number of ways or the probability of its distribution, hence to the level of disorder of the energy.

Equilibrium constant

Equilibrium constant: the ratio of the concentrations (or partial pressures) of reactants over products, each raised to its stoichiometric coefficient, when the system is at equilibrium.

Reaction quotient

Reaction quotient: the value of the equilibrium constant expression under any conditions, not at equilibrium.

Triple point

Triple point: The temperature and pressure at which a substance can exist as a solid, liquid and gas in equilibrium.

• Consider the following reaction.

 $H_2O(g) + Cl_2O(g) \iff 2HOCl(g) \qquad K_p = 0.090 \text{ at } 298 \text{ K}$ Calculate  $\Delta G^{\circ}$  (in J mol<sup>-1</sup>) for this reaction.

 $\Delta G^{\circ} = -RT \ln K_{\rm p} = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(0.090) = 6.0 \times 10^3 \text{ J mol}^{-1}$ 

$$\Delta G^{\circ} = 6.0 \times 10^3 \text{ J mol}^{-1}$$

Calculate the reaction quotient, Q, at 25 °C when  $p(H_2O) = 18$  mmHg,  $p(Cl_2O) = 2.0 \text{ mmHg and } p(HOCl) = 0.10 \text{ mmHg}.$ 

The reaction quotient is given by:

$$Q_{\rm p} = \frac{p({\rm HOCl})^2}{p({\rm H}_2{\rm O})p({\rm Cl}_2{\rm O})} = \frac{(0.10)^2}{(18)(2.0)} = 2.8 \times 10^{-4}$$

$$Q = 2.8 \times 10^{-4}$$

In which direction will the reaction proceed spontaneously at these partial pressures?

As Q < K, the reaction will proceed towards products (i.e. in the forward direction).