

St. Andrew's Junior College H1 Chemistry 2022 Physical Chemistry Tutorial Chemical Equilibrium

Equilibrium constant K_c calculation

1. $N_2(g) + O_2(g) = 2 \text{ NO}(g) \Delta H = + 180 \text{ kJmol}^{-1}$

The equilibrium constant for the reaction above is 6.2×10^{-4} at 2000 °C.

(a) Write down an expression for K_c for the above equilibrium, stating its units.

$$K_{\rm C} = \frac{[\rm NO]^2}{[\rm N_2][\rm O_2]}$$
 Units : no units

(b) A 25 dm³ flask contains 0.27 moles of N₂, 0.001 mole of NO and x moles of O₂ at equilibrium. Calculate the value of x. [Ans: 0.00597 mol]

Concentration of N₂ at equilibrium = $\frac{0.27}{25} = 0.0108 \text{ mol dm}^{-3}$ Concentration of O₂ at equilibrium = $\frac{x}{25} \text{ mol dm}^{-3}$ Concentration of NO at equilibrium = $\frac{0.001}{25} = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$ $K_{c} = \frac{[NO]^{2}}{[N_{2}][O_{2}]}$ $6.2 \times 10^{-4} = \frac{(0.001)^{2}}{0.27x}$ x = 0.00597 mol

2. N2010 P3 Q2b(iv)

The addition of glucono-delta-lactone, GDL, to soy milk produces a soft form of dofu due to a gradual acidification of the mixture. In aqueous solution the following equilibrium is slowly set up.



When 1.00g of GDL (Mr=178) was dissolved in 50.0cm³ water and the solution allowed to reach equilibrium, the concentration of gluconic acid was found to be 0.0670 mol dm⁻³.

(i) Write an expression for K_c for the equilibrium above, and use the data given to calculate its value. You can assume that $[H_2O] = 55.5 \text{ mol } dm^{-3}$ throughout. [Ans: 0.0266 mol⁻¹ dm³]

Initial [GDL] = $(1.00/178) / 0.050 = 0.1124 \text{ mol dm}^{-3}$

	GDL	H_2O	gluconic acid
Initial conc / mol dm ⁻³	0.1124	55.5	0
Change in conc/ mol dm ⁻³	- 0.0670	0	+0.0670
Equilibrium conc / mol dm ⁻³	0.0454	55.5	0.0670
K _c = [gluconic acid]/ [GDL][H ₂	2 O]		

K_c = <u>0.0266 mol⁼¹ dm</u>³ (3sf)

Le Chatelier's Principle & Equilibrium Position

- 3. [J95/I/2]
 - (a) State Le Chatelier's Principle.
 - (b) In relation to the following equilibria,

Equilibrium 1

 $H_2O(g) + C(s) - H_2(g) + CO(g) \Delta H = + 131 \text{ kJ mol}^{-1}$ Equilibrium 2

 $2 \text{ CrO}_{4^{2-}}(aq) + 2 \text{ H}^{+}(aq) \longrightarrow \text{Cr}_{2}\text{O}_{7^{2-}}(aq) + \text{H}_{2}\text{O}(l)$

Use Le Chatelier's principle to predict and explain the effect on the equilibrium position and K_c on the following changes:

- (i) increasing pressure on Equilibrium 1,
- (ii) increasing the temperature in Equilibrium 1,
- (iii) increasing $[H^+(aq)]$ on Equilibrium 2.
- (a) Le Chatelier's Principle states that if a system at dynamic equilibrium is subjected to a change, the system responds in such a way so as to oppose/counteract the change, and a new equilibrium is formed.
- (b)(i) When pressure is increase in Equilibrium 1, the <u>equilibrium position shifts</u> <u>LEFT</u> to <u>decrease the pressure by decreasing the amount of gaseous</u> <u>particles</u>.

 $K_{\rm c}$ has **<u>no change</u>** as it's only affected by temperature.

- b(ii) When temperature increased in Equilibrium 1, the <u>equilibrium position</u> <u>shifts RIGHT to decrease the temperature</u> by absorbing the additional heat, favouring the endothermic reaction. Since $\underline{K_c} = \underline{k_f} / \underline{k_b}$, when temperature increases, both rate forward and rate backward increases. However, since the <u>forward reaction is</u> <u>favoured, rate forward increases more than the rate backward</u>. Hence, <u> K_c increases</u>.
- b(iii) When [H⁺] increases, the <u>equilibrium position shifts RIGHT to decrease</u> [H[±]].

 $K_{\rm c}$ has $\underline{\text{no change}}$ as its only affected by temperature.

INTEGRATED QUESTION

4. At 200 °C, K_c for the reaction,

$$PCI_{5}(g) \longrightarrow PCI_{3}(g) + CI_{2}(g) \Delta H = + 124 \text{ kJ mol}^{-1}$$

has a numerical value of 8 x 10^{-3} .

(a) Write an expression for K_c for this reaction. State the units for K_c .

$$K_{C} = \frac{[PCI_{3}][CI_{2}]}{[PCI_{5}]}$$
 units: mol dm⁻³

(b) What is the value of K_c for the reverse reaction at 200 °C and what are its units? [Ans: 125]

$$K_{\rm c}$$
 of the reverse reaction = $\frac{1}{[8.0 \times 10^{-3}]}$ = 125 mol⁻¹ dm³

- (c) How would the equilibrium position and the value of K_c change if
 - (i) more PCl_5 is added;

The **position of equilibrium shifts RIGHT** to decrease the amount of PCl_5 . Value of <u>*K*c</u> remains unchanged</u> as it is only affected by temperature.

(ii) the pressure is increased;

The <u>position of equilibrium shifts LEFT</u> to <u>decrease the amount of</u> <u>gas particles</u> so as to decrease pressure. Value of <u> K_c remains unchanged</u> as it is only affected by temperature.

(iii) the temperature is increased?

The <u>equilibrium position shifts RIGHT</u> to <u>absorb the excess heat</u> so as to decrease the temperature by <u>favouring the endothermic</u> <u>reaction</u>. Since $K_c = k_f / k_b$, when temperature increases, both rate forward and rate backward increases. However, since the <u>forward reaction is</u>

favoured, rate forward increases more than the rate backward. Hence, $\underline{K_c \text{ increases.}}$

(d) A sample of pure PCl_5 was introduced into an evacuated vessel at 200°C. When the equilibrium was obtained, the concentration of PCl_5 was 5.0 x 10⁻² mol dm⁻³. What are the concentrations of PCl_3 and Cl_2 at equilibrium? **[Ans: 0.020 mol dm⁻³]**

	PCl_5 (g)		PCl_3 (g)	+ Cl ₂ (g)
Initial conc/ mol dm ⁻³	5.0 x 10 ⁻² + x		0	0
Change / mol dm ⁻³	-X		+ x	+ x
equilibrium conc / mol dm ⁻³	5.0 x 10 ⁻²		x	Х

$$K_{\rm C} = \frac{[{\rm PCI}_3][{\rm CI}_2]}{[{\rm PCI}_5]}$$
$$K_{\rm C} = \frac{x^2}{5.0 \times 10^{-2}}$$
$$8 \times 10^{-3} = \frac{x^2}{5.0 \times 10^{-2}}$$
$$x = 0.020$$

 $[PCl_3] = [Cl_2] = 0.020 \text{ mol dm}^{-3}$

5. 2018 A'level P2/7(c)

Chlorine and bromine are formed when bromine monochloride, BrC*l*, decomposes.

 $2BrCl(g) \iff Br_2(g) + Cl_2(g)$

Measured amounts of each of the gases were mixed and sealed in a container. The mixture was allowed to reach equilibrium at 100°C. The equilibrium concentration of each gas was measured and is shown in Table 7.1.

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Temperature / °C	[BrCl] / mol dm ⁻³	[Br ₂] / mol dm ⁻³	[Cl ₂] / mol dm ⁻³
100	6.26 x 10 ⁻²	1.62 x 10 ⁻³	3.48 x 10 ⁻²

(i) Write the expression for K_c and give its units.

 $K_c = \frac{[Br_2][Cl_2]}{BrCl^2} \frac{[Br_2][Cl_2]}{BrCl^2}$ No units

(ii) Calculate the value of K_c at 100°C. [Ans: 0.0144]

 $K_{c} = \frac{\frac{1.62 \times 10^{-3} \times 3.48 \times 10^{-2}}{(6.26 \times 10^{-2})^{2}} \frac{1.62 \times 10^{-3} \times 3.48 \times 10^{-2}}{(6.26 \times 10^{-2})^{2}}}{(6.26 \times 10^{-2})^{2}} = 0.0144$

(iii) The experiment was repeated at 250°C. The numerical value of K_c was found to be 0.132.

Deduce whether the decomposition reaction is exothermic or endothermic. Explain your answer.

When temperature increases, K_c increases. This meant that forward rate increases more than backward rate. Hence, the forward reaction is favoured and is <u>endothermic</u>.

(iv) The first experiment at 100°C was repeated but the total pressure was doubled.
Predict the effect this would have on the value of *K_c* at 100°C. Explain your answer.
[No calculations are required.]

There is no change in K_c . K_c is only affected by the change in temperature.

6. Two gases, A and B, react as follows.

$$\mathbf{A}(g) + \mathbf{B}(g) \longrightarrow 2\mathbf{C}(g)$$

A mixture containing 1 mole each of **A** and **B** was heated in a closed vessel and the reaction was allowed to reach equilibrium at 400 K. The graph shows how the number of moles of each gas varies with time.



(a) Calculate the value of the equilibrium constant K_c for this reaction at 400 K.[Ans:9]

$$K_{c} = \frac{[C]^{2}}{[A][B]} = \frac{\left(\frac{1.2}{V}\right)^{2}}{\left(\frac{0.4}{V}\right)\left(\frac{0.4}{V}\right)} = 9$$

(b) On reaching equilibrium, an additional 1 mole each of A and B was injected into the vessel and the system was allowed to reach the new equilibrium at the same temperature of 400 K. Calculate the amount of A, B and C at the new equilibrium.

[Ans: A & B = 0.8 mol, C = 2.4 mol]

Let the change in number of moles of **A** be x.

Initial mole / mol Change in mole / mol Final mole / mol	A + 1.4 -x (1.4 - x)	B 1.4 -x (1.4 –	x)	2 C 1.2 +2x (1.2 + 2x	.)
$\frac{\left(\frac{1.2+2x}{V}\right)^2}{\left(\frac{1.4-x}{V}\right)\left(\frac{1.4-x}{V}\right)} = K_c =$	9				
$\frac{1.2 + 2x}{1.4 - x} = +3$					
x = 0.6					
No of moles of A and B at	new equil	ibrium =	= 1.4	0.6 = 0.8	mol

No of moles of **C** at new equilibrium = 1.2 + 2(0.6) = 2.4 mol

(c) Extend the graph and include the sketch of how the no of moles of the gases change with time when 1 mole each of **A** and **B** were later injected into the vessel.



7. 2015 A'level P2/5(d)

When sulfur is reacted with fluorine, a mixture of SF_4 and SF_6 is formed.

However, when sulfur is reacted with oxygen, sulfur dioxide, SO₂, is the only product formed.

Under room conditions, SO_2 then reacts slowly with oxygen to produce sulfur trioxide, SO_3 . The following equilibrium is established.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -197 \text{ kJ mol}^{-1}$$

Industrially, SO₃ is produced from SO₂ by reacting it with oxygen under the following conditions.

pressure	2atm (202kPa)
temperature	450°C
catalyst	V ₂ O ₅

*Note: Though this question takes reference from the industrial conditions of the production of SO_3 , it did not ask to justify why this conditions are used but how these industrial conditions affect the position of equilibrium. Hence, these industrial conditions will take reference from room temperature and pressure and hence the industrial conditions are considered as high temperature and high pressure.

 A <u>high pressure</u> would <u>shift the position of the equilibrium</u> to the <u>right</u> to lower pressure by favoring the side with less amount of gas molecules or particles. At the same time, high pressure will lead to an <u>increase</u> in the <u>rate of</u> **<u>reaction</u>** (as there are more particles per unit volume leading to an increase in frequency of effective collision)

- A <u>high temperature</u> would <u>shift the position of the equilibrium</u> to the <u>left</u> to lower temperature by favor the endothermic reaction to absorb the additional heat. At the same time, high temperature will lead to an <u>increase</u> in the <u>rate of</u> <u>reaction</u> as well (as the kinetic energy of the particles increase leading to an increase in frequency of effective collision)
- A catalyst <u>does not affect</u> the <u>position of equilibrium</u>. However, a catalyst does <u>increase the rate</u> of both the forward and backward <u>reaction</u> (as it provides an alternative pathway with lower activation leading to an increase in frequency of effective collion)