

SLE155 Chemistry for the Professional Sciences

Burwood and Geelong



Class 3

Chemical Equilibrium

We will be covering chapter 9

Reversibility of reactions

Chemical equilibrium

Equilibrium constant expressions

K_c and Q_c

Heterogenous equilibrium

Equilibrium and Gibbs energy

Le Chatelier's principle

Equilibrium calculations, ICE table

~~Weak acids and Bases~~

Buffers and titrations



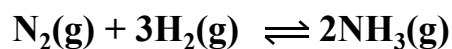
Reversible Reactions

In a **reversible reaction**, there is both a forward and a reverse reaction.

The reversible reaction is written with a double arrow.



Chemical equilibrium



Rates of the forward (left to right) and reverse (right to left) reactions are **equal**.

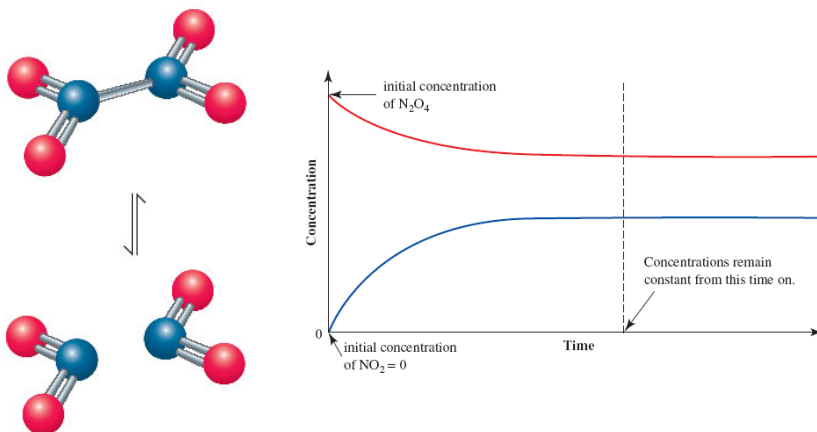
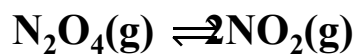
There is no net change in the overall composition of the reaction mixture.

This is called **dynamic equilibrium**.

‘Reactants’ substances are on the left, and

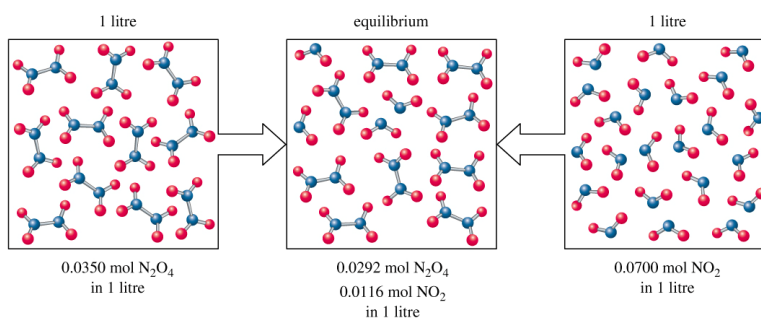
‘Products’ substances are on the right of the chemical equation, joined by special arrows.

Chemical equilibrium



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Chemical equilibrium



**For a given OVERALL system composition
equilibrium concentrations do not depend on
direction of approach.**

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The equilibrium constant, K , and the reaction quotient, Q

For the general reaction $aA + bB \rightleftharpoons cC + dD$

the reaction quotient is

$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Q_c is for systems at any time during the reaction, not necessarily at equilibrium



The equilibrium constant, K , and the reaction quotient, Q

For the general reaction $aA + bB \rightleftharpoons cC + dD$

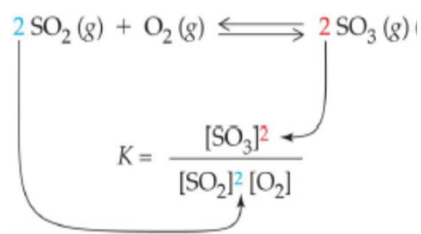
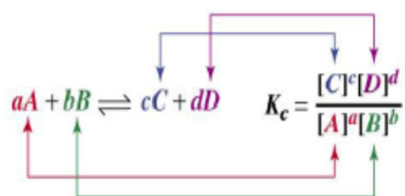
$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad K_c = \frac{[C]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b}$$

Q_c is for systems at any time during the reaction, not necessarily at equilibrium

K_c can have **only one** positive value at a specific temperature but Q_c can have **any** positive value



Equilibrium Constant expression



Kc and Kp

Reactions in solution: Kc is calculated from molar concentrations.

Gaseous reactions: Kp is calculated using partial pressures expressed in Pa

Manipulating equilibrium constant expressions

When the direction of an equation is reversed, the new equilibrium constant is the reciprocal of the original, i.e., 1/original



$$K_c' = \frac{1}{K_c}$$

Manipulating equilibrium constant expressions

When the coefficients in an equation are multiplied by a factor, the equilibrium constant is raised to a power equal to that factor.



$$K_c'' = K_c^2$$

Manipulating equilibrium constant expressions

When chemical equilibria are added, their equilibrium constants are multiplied.



$$\frac{\cancel{[\text{N}_2\text{O}]^2}}{[\text{N}_2]^2 [\text{O}_2]} \times \frac{[\text{NO}_2]^4}{\cancel{[\text{N}_2\text{O}]^2} [\text{O}_2]^3} = \frac{[\text{NO}_2]^4}{[\text{N}_2]^2 [\text{O}_2]^4} \quad K_{c1} \times K_{c2} = K_{c3}$$

The size of the equilibrium constant

Product concentrations are in the numerator (top line) of K_c

The size of K_c gives a measure of how far the reaction proceeds towards completion when equilibrium is reached

The size of the equilibrium constant

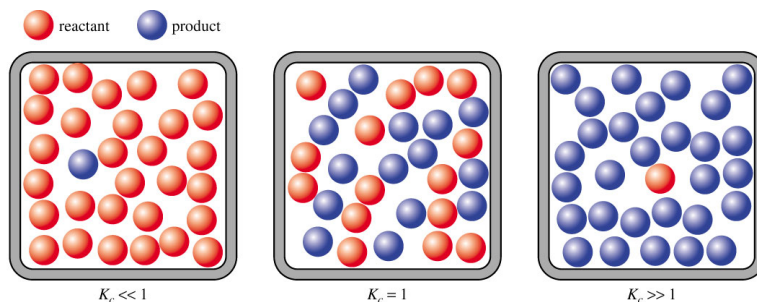


Figure 9.5,

The size of the equilibrium constant is a measure of the **extent of the reaction at equilibrium**.

A **high** value for the equilibrium constant indicates that the reaction will be virtually **complete** at equilibrium.

A **low** value means the reaction has **hardly started**.



Equilibrium constant expressions for heterogeneous systems

For any pure liquid or solid at constant temperature, the ratio of amount (number of moles) of substance to volume of substance is constant.



1 mol NaHCO_3
38.9 mL

$$\text{concentration} = \frac{1 \text{ mol NaHCO}_3}{0.0389 \text{ L}} = 25.7 \text{ mol L}^{-1}$$



2 mol NaHCO_3
77.8 mL

$$\text{concentration} = \frac{2 \text{ mol NaHCO}_3}{0.0778 \text{ L}} = 25.7 \text{ mol L}^{-1}$$



Equilibrium constant expressions for heterogeneous systems

Heterogeneous reaction means that more than one phase exists in reaction mixture



$$K_c = [\text{H}_2\text{O}(\text{g})][\text{CO}_2(\text{g})]$$

Do not include concentrations of pure solids or pure liquids



Equilibrium and Gibbs free energy

ΔG and spontaneity

Spontaneity of a chemical or physical process at constant temperature and pressure can be predicted from the sign of the Gibbs energy change.

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

$\Delta G < 0$: the process is spontaneous

$\Delta G > 0$: the process is nonspontaneous

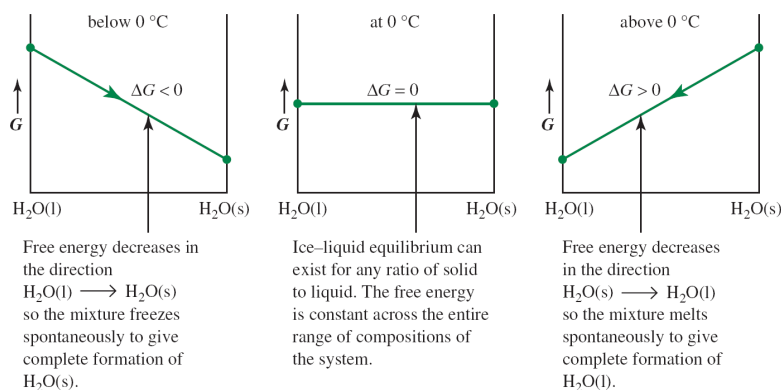
$\Delta G = 0$: the system is at equilibrium



Equilibrium and Gibbs free energy

Free energy diagrams

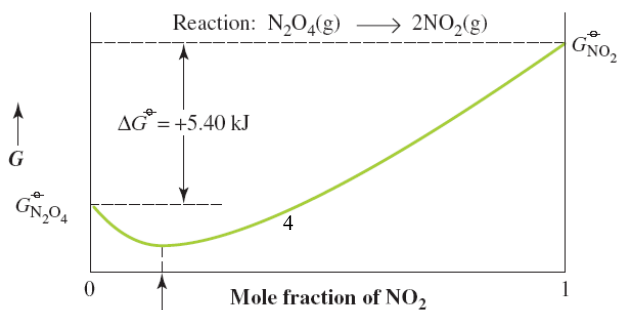
Phase changes



Equilibrium and Gibbs free energy

Free energy diagrams

Chemical reactions



Equilibrium occurs here at a total pressure of $1.013 \times 10^5 \text{ Pa}$ with about 16.6% of the N_2O_4 decomposed.



Equilibrium and Gibbs free energy

The relationship between ΔG^θ and K

$$\Delta G = \Delta G^\theta + RT \ln Q$$

R is the gas constant, $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

T is the temperature in kelvin

$\ln Q$ is the natural logarithm of the reaction quotient

Gaseous reactions: Q is calculated using partial pressures expressed in Pa

Reactions in solution: Q is calculated from molar concentrations



Chapter 9

Equilibrium and Gibbs free energy

$$\Delta G = \Delta G^\theta + RT \ln Q$$

If the system is at equilibrium

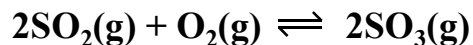
$$\Delta G = 0 \text{ and } Q = K$$

$$0 = \Delta G^\theta + RT \ln K$$

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



Equilibrium and Gibbs free energy



$\Delta G^\theta = -1.40 \times 10^2 \text{ kJ mol}^{-1}$ for this reaction at 25 °C.

What is the value of K_p at this temperature?

$$\ln K_p = \frac{-\Delta G^\theta}{RT}$$

$$K_p = e^{56.5}$$

$$K_p = 3 \times 10^{24}$$

$$\ln K_p = \frac{-(-1.40 \times 10^5 \text{ J mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}$$

$$\ln K_p = +56.5$$



ΔG as a predictor of reaction outcome

If $\Delta_r G^\theta$ is large and negative, K is big. This means the reaction will favour the product(s).

If $\Delta_r G^\theta$ is large (i.e. $> 20 \text{ kJ mol}^{-1}$) and positive, K is small. This means reactants are favoured and almost no reaction occurs (at room temperature).

The sign and size of $\Delta_r G^\theta$ indicate whether a spontaneous reaction will occur and to what degree.



ΔG as a predictor of reaction outcome

The relationship between ΔG^θ and K

Thermodynamic data collected at 25 °C may be used to calculate the values of equilibrium constants at temperatures other than 25 °C

Values of ΔH^θ and ΔS^θ do not change much with temperature



LeChâtelier's Principle

Any change in equilibrium conditions upsets the equilibrium of the system.

A system at equilibrium under stress will shift to relieve the stress.

The rate of the forward or reverse reaction will change to return the system to equilibrium.



Systems at equilibrium respond to change

Le Châtelier's principle

If an outside influence upsets an equilibrium, the system undergoes a change in a direction that counteracts the disturbing influence and, if possible, returns the system to equilibrium

Compare equilibrium constant, K , and reaction quotient, Q , when examining the effect of perturbation to a chemical process at equilibrium.



Systems at equilibrium respond to change

Adding or removing a product or reactant

When not a pure solid or liquid, removal or addition of a reactant or product instantaneously alters the concentration of that species in the reaction mixture

The value of Q changes so that $Q \neq K$, the system is no longer at equilibrium



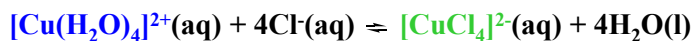
Systems at equilibrium respond to change

Adding or removing a product or reactant

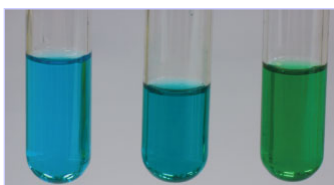
$Q = K$ equilibrium

$Q < K$ shift towards products

$Q > K$ shift towards reactants



$$Q = \frac{[\text{CuCl}_4^{2-}]}{[\text{Cu}(\text{H}_2\text{O})_4^{2+}] [\text{Cl}^{-}]^4}$$



Systems at equilibrium respond to change

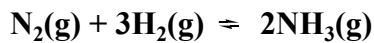
Changing the pressure in gaseous reactions

Two ways of changing the total pressure

Changing the volume of the system

Adding an inert gas

Consider the equilibrium



$$Q_p = \frac{\left(\frac{p_{\text{NH}_3}}{p^\theta}\right)^2}{\left(\frac{p_{\text{N}_2}}{p^\theta}\right)\left(\frac{p_{\text{H}_2}}{p^\theta}\right)^3}$$

Systems at equilibrium respond to change

Changing the pressure in gaseous reactions

Changing the volume of the system

$$Q_p = \frac{\left(\frac{p_{\text{NH}_3}}{p^\theta}\right)^2}{\left(\frac{p_{\text{N}_2}}{p^\theta}\right)\left(\frac{p_{\text{H}_2}}{p^\theta}\right)^3} \quad Q_c = \frac{\frac{(n_{\text{NH}_3})^2}{V^2}}{\frac{n_{\text{N}_2}}{V} \times \frac{(n_{\text{H}_2})^3}{V^3}} \quad c = \frac{n}{V}$$
$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \quad Q_c = \frac{(n_{\text{NH}_3})^2}{n_{\text{N}_2} \times (n_{\text{H}_2})^3} \times V^2$$

Increasing the volume reduces the partial pressures. The side with the greater number of gas molecules will be favoured.

Systems at equilibrium respond to change

Changing the pressure in gaseous reactions

Adding an inert gas

Increases total pressure of system

Does not alter the position of equilibrium

Add helium to $\text{N}_2/\text{H}_2/\text{NH}_3$ equilibrium mixture

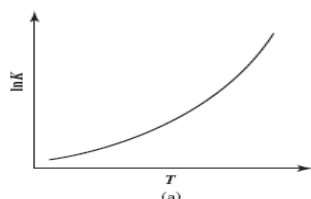
Does not react with products or reactants

Q_p is not changed

$$Q_p = \frac{\left(\frac{p_{\text{NH}_3}}{p^\theta}\right)^2}{\left(\frac{p_{\text{N}_2}}{p^\theta}\right)\left(\frac{p_{\text{H}_2}}{p^\theta}\right)^3}$$

Systems at equilibrium respond to change

Changing the temperature of a reaction mixture

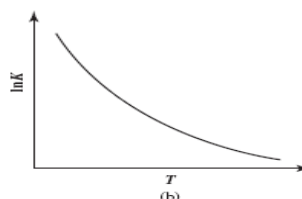


ΔH° is positive

Endothermic

$$Q < K$$

Products are favoured



ΔH° is negative

Exothermic

$$Q > K$$

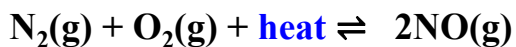
Reactants are favoured



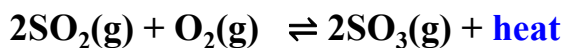
Systems at equilibrium respond to change

Remember

Endothermic



Exothermic



Treat enthalpy like a reactant or product



Systems at equilibrium respond to change

Addition of a catalyst

Catalysts affect the rates of chemical reactions without being used up

Addition of a catalyst may help bring a system to chemical equilibrium more rapidly

Addition of a catalyst does **not** affect the **position** of equilibrium



Equilibrium calculations

Calculating K_c from equilibrium concentrations

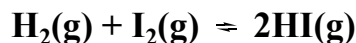
Measure the concentrations of reactants and products after equilibrium reached

Substitute these equilibrium values into the equilibrium constant expression to calculate K_c



Equilibrium calculations

At a certain temperature, a mixture of H_2 and I_2 was prepared by placing 0.200 mol of H_2 and 0.200 mol I_2 into a 2.00 litre flask. After a period of time, the equilibrium:



was established. The purple colour of the I_2 vapour was used to monitor the reaction, and it was determined that, at equilibrium, the I_2 concentration had dropped to 0.020 mol L^{-1} .

What is the value of K_c for this reaction at this temperature?

Equilibrium calculations

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$\left(\begin{array}{c} \text{equilibrium} \\ \text{concentration} \end{array} \right) = \left(\begin{array}{c} \text{initial} \\ \text{concentration} \end{array} \right) + \left(\begin{array}{c} \text{change in} \\ \text{concentration} \end{array} \right)$$

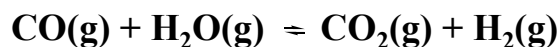
	$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$		
Initial concentration (mol L^{-1})	0.100	0.100	0.000
Change in concentration (mol L^{-1})	-0.080	-0.080	+2(0.080)
Equilibrium concentration (mol L^{-1})	0.020	0.020	0.160

$$K_c = \frac{(0.160)^2}{(0.020)(0.020)}$$

$$K_c = 64$$

Equilibrium calculations

The water-gas shift reaction:



has $K_c = 4.06$ at 500°C .

If 0.100 mol of CO and 0.100 mol of $\text{H}_2\text{O(g)}$ are placed in a 1.00-litre reaction vessel at this temperature, what are the concentrations of the reactants and products when the system reaches equilibrium?



Equilibrium calculations

$$K_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = 4.06$$

	CO(g) + H ₂ O(g)		⇌ CO ₂ (g) + H ₂ (g)	
Initial concentration (mol L ⁻¹)	0.100	0.100	0.0	0.0
Change in concentration (mol L ⁻¹)	-x	-x	+x	+x
Equilibrium concentration (mol L ⁻¹)	0.100-x	0.100-x	x	x

$$K_c = \frac{(x)(x)}{(0.100-x)(0.100-x)} = 4.06$$

$$\frac{x^2}{(0.100-x)^2} = 4.06$$

$$\frac{x}{(0.100-x)} = \sqrt{4.06} = 2.01$$

$$x = 2.01(0.100 - x)$$

$$x = 0.201 - 2.01x$$

$$x + 2.01x = 0.201$$

$$3.01x = 0.201$$

$$x = 0.0668$$



Equilibrium calculations

$$[\text{CO}] = 0.100 - x = 0.100 - 0.0668 = 0.033\text{M}$$

$$[\text{H}_2\text{O}] = 0.100 - x = 0.100 - 0.0668 = 0.033\text{M}$$

$$[\text{CO}_2] = x = 0.0668\text{M}$$

$$[\text{H}_2] = x = 0.0668\text{M}$$

$$Q_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]}$$

$$Q_c = \frac{(0.0668)^2}{(0.033)^2} = 4.1$$

Rounding K_c to 2 significant figures gives 4.1, so the calculated concentrations are correct.

Chapter 9 Summary

$\Delta G = 0$ at equilibrium.

Equilibrium is the point at which the reaction appears to have stopped, there is no further change in concentrations of reactants or products.

At equilibrium the rates of the forward and reverse reactions are equal.

Equilibrium reactions are identified by a double-headed arrow.

Chapter 9 Summary

- The equilibrium constant, K , quantifies the equilibria.



- The following holds when equilibrium is established:

$$K_c = \frac{[C]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b}$$

- K_c dependent on temperature, temperature must always be specified when K_c is reported.
- K is dimensionless (it does not have units).



Chapter 9 Summary

The reaction quotient, Q , for the reaction:



$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The concentrations are not necessarily equilibrium concentrations.

Q and K can be compared to determine which direction (forward or reverse) will be favoured so $Q = K$.



Chapter 9 Summary

- When a reaction is reversed its K value is inverted to become $1/K$.
- When the stoichiometric coefficients are multiplied by a factor, the new K is the old K raised to a power of the same factor.
- When reactions are added together their K values are multiplied.
- If $K > 1$, product is favoured, if $K < 1$, reactant is favoured.
- Pure solids and pure liquids are not included in the equilibrium constant expression or the reaction quotient expression.



Chapter 9 Summary

Le Chatelier's principle:

If an outside influence upsets an equilibrium, the system undergoes a change in a direction that counteracts the disturbing influence and, if possible, returns the system to equilibrium.

Only a change of temperature can change the value of K .

