CHEM 191
Energetics & Equilibria in Biological Systems
Module 1 Lecture 3
Equilibrium

Brown (15th) Chapter 15

1

Module 1 Lecture 3
Learning objectives

- to be able to write the correct expressions for Q and K_c
- to understand the difference between Q and K_c
- to understand the information about an equation K_c provides
- to be able to do problems involving equilibrium

2

Chemical reactions

In some cases, when a chemical reaction occurs the reaction continues until all of the reactants have been converted into products.

We say such a reaction has **'gone to completion'**

But this is not always the case.

3

Reaction quotient

In order to determine if a reaction has gone to completion or not, we need a way to quantify the amounts of the reactants and products present in the reaction mixture over time - **Reaction Quotient *Q***

For the general reaction

aA + bB → cC + dD

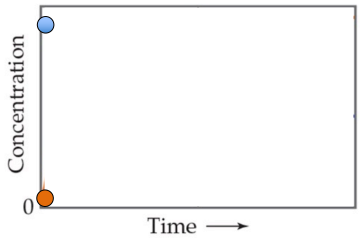
$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

[ ] represents concentrations

Concentration terms raised to the power of the stoichiometric coefficients.

Lets look at the reaction $\mathbf{N_2O_4(g) \rightarrow 2NO_2(g)}$

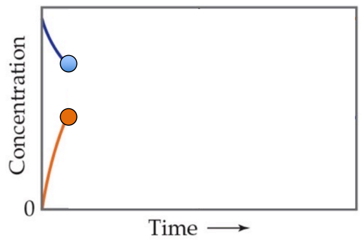
4



At time = 0 (ie before the reaction starts)

$[N_2O_4]$ = 1 mol L^{-1} $[NO_2]$ = 0 mol L^{-1}

$$Q = \frac{[NO_2]^2}{[N_2O_4]} = 0$$

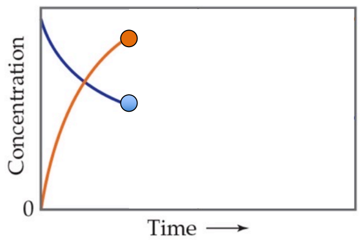


At time = 5 min

$[N_2O_4]$ = 0.8 mol L^{-1} $[NO_2]$ = 0.4 mol L^{-1}

$$Q = \frac{[NO_2]^2}{[N_2O_4]} = \frac{[0.4]^2}{[0.8]} = 0.2$$

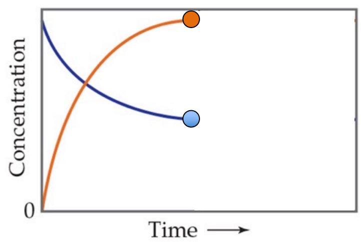
5



At time = 10 minutes

$[N_2O_4]$ = 0.6 mol L^{-1} $[NO_2]$ = 0.8 mol L^{-1}

$$Q = \frac{[NO_2]^2}{[N_2O_4]} = \frac{[0.8]^2}{[0.6]} = 1.07$$

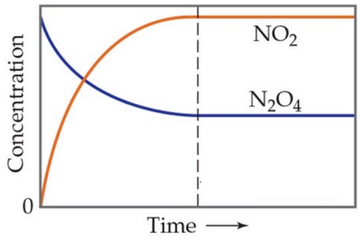


At time = 20 min

$[N_2O_4]$ = 0.45 mol L^{-1} $[NO_2]$ = 1.1 mol L^{-1}

$$Q = \frac{[NO_2]^2}{[N_2O_4]} = \frac{[1.1]^2}{[0.45]} = 2.7$$

6



At time = 30 minutes

[N_2O_4] = 0.45 mol L^{-1} [NO_2] = 1.1 mol L^{-1}

$$Q = \frac{[NO_2]^2}{[N_2O_4]} = \frac{[1.1]^2}{[0.45]} = 2.7 \text{ still!}$$

After some point in time the value of *Q* stops increasing.

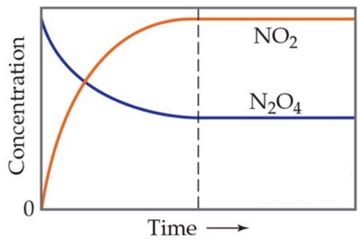
BUT the reaction has NOT gone to completion – there are still reactant molecules present

So what is happening here?

7

At the point where *Q* stops increasing, the reaction converting N_2O_4 into NO_2 is still happening

But as quickly as NO_2 molecules are being formed, other NO_2 molecules are being converted back into N_2O_4 molecules.



So the reaction is going both ways at the same time.

We say that it is at **EQUILIBRIUM** $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

8

Dynamic Equilibrium

9

The equilibrium constant

- We can quantify a system **at equilibrium** by using the equilibrium constant K_c
  At equilibrium $\boldsymbol{Q_e = K}$

- For the general equilibrium

$$\mathbf{aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)}$$

the equilibrium constant can be defined in terms of concentrations (K_c)

$$K_c = \frac{\left(\frac{[C]}{c^o}\right)^c \left(\frac{[D]}{c^o}\right)^d}{\left(\frac{[A]}{c^o}\right)^a \left(\frac{[B]}{c^o}\right)^b}$$

c^o = ‘standard concentration = 1 mol L^{-1}.

10

The equilibrium constant

So we can simplify expressions for K_c

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

So for our **$N_2O_4(g) \rightleftharpoons 2NO_2(g)$** reaction we would have

$$Q_e = K_c = \frac{[NO_2]_e^2}{[N_2O_4]_e} = 2.7$$

Note that the subscript 'e's signify the concentrations at equilibrium

11

Note in the previous example, the value of *Q* increased until equal to *K*

In general when the ***Q*** of a reaction mixture **is less than** the value of ***K*** for the reaction, **reactants are converted into products** until equilibrium is reached.
Q < K $\rightarrow$

The opposite is also true – if the value of ***Q*** for a reaction mixture **is greater than** the value of ***K*** for the reaction, **products are converted back into reactants** until equilibrium is reached.
Q > K $\leftarrow$

So, for example, the equilibrium composition of the N_2O_4/NO_2 mixture is the same, regardless of whether we start with pure N_2O_4, or with pure NO_2.

***K* only depends on temperature but not on the starting concentrations.**

12

The Equilibrium constant K_c

- Write the equilibrium constant expressions K_c for the reaction

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

$$K_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$$

- Always make sure products are on the top line and reactants on the bottom
- Remember to raise the concentrations to the powers of their stoichiometric coefficients.

13

Learn

Products raised to stoichiometric powers

Divided by reactants raised to theirs

Pure solids and pure liquids do not appear

14

The magnitude of *K*

- The value of *K* (generally given at 25 °C) gives information about the extent of reaction at equilibrium
- e.g. for $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$ $K_c = \frac{[H_2O]^2}{[H_2]^2[O_2]} = 9.1\times10^{80} = \frac{9.1\times10^{80}}{1}$

  and the reaction goes essentially to completion. The position of equilibrium lies far to the right.
- for $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_c = \frac{[NO]^2}{[N_2][O_2]} = 4.8\times10^{-31} = \frac{4.8}{10^{31}}$

  and the reaction barely begins when equilibrium is established. The position of equilibrium lies far to the left

15

Writing *K* expressions

- Pure solids and pure liquids *never* appear in an equilibrium constant expression. This is because the concentration of a solid or a liquid is constant.
- e.g. for

  $2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + H_2O(g) + CO_2(g)$

  $K_c = [H_2O][CO_2]$

Note that H_2O here is a gas so it is included

and for

$CaO(s) + SO_2(g) \rightleftharpoons CaSO_3(s)$ $K_c = \frac{1}{[SO_2]}$

16

Quantifying equilibria

- How do we do quantitative calculations on systems at equilibrium or perturbed from equilibrium?
- Calculate K_c for the equilibrium **$N_2O_4(g) \rightleftharpoons 2NO_2(g)$** at 298 K given the following equilibrium concentrations:
  $[N_2O_4]_e = 0.0292$ mol L^{-1}, $[NO_2]_e = 0.0116$ mol L^{-1}.

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.0116)^2}{(0.0292)} = 4.61 \times 10^{-3}$$

- Equilibrium position lies to the left. Remember that K_c has no units.

17

Calculating *K* – example 1

- 0.100 mol $H_2(g)$ and 0.100 mol $I_2(g)$ were placed in a 1.00 L flask. When equilibrium was established, $[I_2] = 0.020$ mol L^{-1}. What is K_c for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

- To solve this, set up a ***concentration or ICE table.*** (this needs practice)
- Summarise what we know

	$H_2(g)$	$I_2(g)$	$HI(g)$
Initial (mol L^{-1})	0.100	0.100	0.00
Change (mol L^{-1})			
Equilm (mol L^{-1})		0.020	

18

Calculating *K* – example 1

- Change in amount of I_2 = 0.100 – 0.020 = **0.080** mol
  so 0.080 mol of I_2 used up i.e. **-0.080** mol

- From stoichiometry change in amount of I_2 must equal change in amount of H_2 = **0.080** mol. (If 0.080 mol of I_2 reacted then 0.080 mol of H_2 must react as well)

	$H_2(g)$	$I_2(g)$	$HI(g)$
Initial (mol L^{-1})	0.100	0.100	0.00
Change (mol L^{-1})	**-0.080**	**-0.080**	
Equilm (mol L^{-1})		0.020	

19

Calculating *K* – example 1

- If 0.080 mol I_2 reacted, it will produce (from stoichiometry of equation)

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

2 × 0.080 mol HI thus the change in HI = **0.160** mol

	$H_2(g)$	$I_2(g)$	$HI(g)$
Initial (mol L^{-1})	0.100	0.100	0.00
Change (mol L^{-1})	**-0.080**	**-0.080**	**0.160**
Equilm (mol L^{-1})		0.020	

20

Calculating K – example 1

- Can now complete table to work out equilibrium concentrations in the 1.00 L flask

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.160)^2}{(0.020)(0.020)} = 64$$

	$H_2(g)$	$I_2(g)$	$HI(g)$
Initial (mol L^{-1})	0.100	0.100	0.00
Change (mol L^{-1})	**-0.080**	**-0.080**	**0.160**
Equilm (mol L^{-1})	**0.020**	0.020	**0.160**

21

Calculating K – example 2

- 0.200 mol $N_2(g)$ and 0.600 mol $H_2(g)$ were placed in a 1.00 L flask. When equilibrium was established, $[NH_3]$ = 0.0032 mol L^{-1}. What is K_c for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

- Summarise what we know

	$N_2(g)$	$H_2(g)$	$NH_3(g)$
Initial (mol L^{-1})	0.200	0.600	0.00
Change (mol L^{-1})			
Equilm (mol L^{-1})			0.00320

22

Calculating *K* – example 2

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

- If **0.00320** mol NH_3 produced then (using stoichiometry of equation) amount of N_2 reacting = ½ × 0.00320 = **0.00160** mol
- Amount of H_2 reacting = 3/2 × 0.00320 = **0.00480** mol

	$N_2(g)$	$H_2(g)$	$NH_3(g)$
Initial (mol L^{-1})	0.200	0.600	0.00
Change (mol L^{-1})	**-0.00160**	**-0.00480**	**0.00320**
Equilm (mol L^{-1})			0.00320

23

Calculating *K* – example 2

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

- Thus amount of N_2 remaining at equilibrium = 0.200 – 0.00160 = **0.198** mol
- And amount of H_2 remaining at equilibrium = 0.600 – 0.00480 = **0.595** mol

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.00320)^2}{(0.198)\ (0.595)^3} = 2.46 \times 10^{-4}$$

	$N_2(g)$	$H_2(g)$	$NH_3(g)$
Initial (mol L^{-1})	0.200	0.600	0.00
Change (mol L^{-1})	**-0.00160**	**-0.00480**	**0.00320**
Equilm (mol L^{-1})	**0.198**	**0.595**	0.00320

24

Response to change

- How does a system at equilibrium respond to change in
  - amounts of reactants or products
  - pressure

- Can use **Le Châtelier's principle** to determine these:
  - "if a system at equilibrium is disturbed, it will move in such a way to counteract the disturbance and restore equilibrium"

- But this can sometimes be misleading - best to do these types of problems in terms of a comparison of *Q* and *K*.

25

✱ Homework ✱

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Problems 15.5, 15.16, 15.17, 15.18, 15.54

Answers on Blackboard

26