Highlights of last lecture

Oxides of nitrogen

- $\text{N}_2\text{O}$, NO, NO$_2$, NO$_3$ + dimers: $\text{N}_2\text{O}_2$, $\text{N}_2\text{O}_3$, $\text{N}_2\text{O}_4$, $\text{N}_2\text{O}_5$

Role of nitrogen oxides in the atmosphere

- NO$_x$
- HNO$_3$ (acid rain)
- PAN

Greenhouse effect

- Energy balance
- Radiation trapping by atmospheric gases
- Relationship between increasing gases and temperature
Equilibrium

Themes: controlling equilibrium
atmospheric equilibria
commercial production of chemicals

Key thematic concepts:
• Most chemical reactions exist in a state of equilibrium;
• The equilibrium state can be calculated and controlled;
• Industry and biology both take advantage of equilibria;
Equilibrium

Key chemical concepts:
- Equilibrium as a dynamic process;
- Equilibrium constants;
- Direction of chemical change;
- Disturbing equilibrium: Le Chatelier’s principle;

Calculations:
- Calculating equilibrium position;
- Calculating direction of chemical change;
- Calculating new equilibrium after change;
Equilibrium

Last lecture we saw a couple of important atmospheric (smog) reactions that proceeded both L-R and R-L

1. \[ 2 \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4 \]
2. \[ \text{H}_2\text{C}=\text{O}-\cdot + \cdot\text{NO} \rightleftharpoons \text{H}_2\text{C}=\text{O}-\text{NO} \]

Many others, e.g. in ozone depletion:

3. \[ 2 \text{NO} + \text{Cl}_2 \rightleftharpoons 2 \text{NOCl} \]
4. \[ \text{Cl} + \text{O}_2 \rightleftharpoons \text{ClO}_2 \]

Theme of this lecture: Exploring the “equilibrium state” using atmospheric reactions as examples.
NO$_2$ dimerization from last lect.

Start with N$_2$O$_4$(g)...

\[ \text{N}_2\text{O}_4 \ (g) \ \leftrightarrow \ 2 \ \text{NO}_2 \ (g) \]

N$_2$O$_4$ (colourless)

NO$_2$ (brown)

Silberberg, p.715

No further change...
$\text{NO}_2$ dimerization from last lect.

No further change...
Dynamic Equilibrium

- Equilibrium conc’ns do not depend on the starting composition.

\[ \text{N}_2\text{O}_4 (g) \quad \rightleftharpoons \quad 2 \text{NO}_2 (g) \]
Kinetics and equilibrium

\[ \text{N}_2\text{O}_4 (g) \quad \rightleftharpoons \quad 2 \text{NO}_2 (g) \]

rate of forward reaction = rate of reverse reaction

[reactant] and [products] are constant...

This DOES NOT mean the reaction has stopped!
Thermodynamics and equilibrium

Exothermic reactions tend to favour products

Endothermic reactions tend to favour reactants
Three people did an experiment on the equilibrium of this reaction:

\[
N_2O_4 (g) \rightleftharpoons 2 NO_2 (g)
\]

<table>
<thead>
<tr>
<th>Expt</th>
<th>[NO₂] (init.)</th>
<th>[N₂O₄] (init.)</th>
<th>[NO₂] (final)</th>
<th>[N₂O₄] (final)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.1000</td>
<td>0.1018</td>
<td>0.0491</td>
</tr>
<tr>
<td>2</td>
<td>0.1000</td>
<td>0</td>
<td>0.0627</td>
<td>0.0185</td>
</tr>
<tr>
<td>3</td>
<td>0.0500</td>
<td>0.0500</td>
<td>0.0837</td>
<td>0.0332</td>
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Who is right?
Or... what’s the point?
The fundamental observation of chemical equilibrium was first stated in 1864 by two Norwegian chemists, Guldberg and Waage:

“At a given temperature, a chemical system reaches a state in which a particular ratio of reactant and product concentrations has a constant value.”

\[ A + B \rightleftharpoons C + D \]

\[ K_{eq} = \frac{[C] \times [D]}{[A] \times [B]} = \frac{\Pi [\text{products}]}{\Pi [\text{reactants}]} \]

\[ \Pi = \text{“product of”}, \quad \Sigma = \text{“sum of”} \]
Equilibrium constant

\[ \text{N}_2\text{O}_4 \rightleftharpoons \text{NO}_2 + \text{NO}_2 \]

\[ K_{eq} = \frac{[\text{NO}_2] \times [\text{NO}_2]}{[\text{N}_2\text{O}_4]} \]

In general, \( a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D} \);

\[ K_{eq} = \frac{[\text{D}]^d \times [\text{C}]^c}{[\text{A}]^a \times [\text{B}]^b} \]
NO₂ dimerization from last lect.

\[ \text{N}_2\text{O}_4 (g) \rightleftharpoons 2 \text{NO}_2 (g) \]

Three people did an experiment on the equilibrium of this reaction...

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<td>0.0491</td>
<td>0.211 mol/L</td>
</tr>
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<td>0.1000</td>
<td>0</td>
<td>0.0627</td>
<td>0.0185</td>
<td>0.212 mol/L</td>
</tr>
<tr>
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<td>0.0837</td>
<td>0.0332</td>
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So... they were all correct, and the point is that the eq'm position in ALL cases is given by:

\[
\frac{[\text{NO}^2]^2}{[\text{N}_2\text{O}_4]} = 0.211 \text{ mol/L}
\]
Position of eq’m and K

Three examples:

\[ \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g) \quad K_{eq} = 1 \times 10^{-30} \]
\[ 2\text{CO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{CO}_2(g) \quad K_{eq} = 2.2 \times 10^{22} \text{ L/mol} \]
\[ \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \quad K_{eq} = 0.211 \text{ mol/L} \]

Q: Which compounds are favoured at equilibrium?

Hint: remember that \( K = \Pi[\text{prod.}] / \Pi[\text{react.}] \)
The reaction quotient, Q, is calculated in exactly the same way as K, except using current concentrations rather than eq’m concentrations.

\[ 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) \quad K_{eq} = 4.34 \text{ L/mol} \]

I put the following concentrations into a flask:

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</tr>
<tr>
<td>SO₃</td>
<td>3.00</td>
<td>0.350</td>
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Is the reaction at eq’m? If not, which way will it move to achieve eq’m?
The Reaction Quotient

e.g. $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$

$K_{eq} = 4.34 \text{ L/mol}$

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Expt 1:
The reaction quotient, Q, is calculated in exactly the same way as K, except using current concentrations rather than eq'm concentrations.
The Reaction Quotient

e.g. \(2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})\) \(K_{eq} = 4.34 \text{ L/mol}\)

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Expt 2: class problem...
Stoichiometry and Units

\[ \text{N}_2\text{O}_4 (g) \rightleftharpoons 2 \text{NO}_2 (g) \]

expt 1: \[ [X]_{eq} = 0.0491 \quad 0.1018 \text{ mol/L} \]

\[ K_{eq} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 0.211 \text{ mol/L} \]

But, what if I wrote:

\[ \frac{1}{2} \text{N}_2\text{O}_4 (g) \rightleftharpoons \text{NO}_2 (g) \]

expt 1: \[ [X]_{eq} = 0.0491 \quad 0.1018 \text{ mol/L} \]

Or, what if I wrote:

\[ 2 \text{NO}_2 (g) \rightleftharpoons \text{N}_2\text{O}_4 (g) \]

expt 1: \[ [X]_{eq} = 0.1018 \quad 0.0491 \text{ mol/L} \]
Stoichiometry and Units

The eq’m constant must be associated with a specific stoichiometric chemical eq’n.

- If you multiply the stoichiometry by n, you change K by a power of n
- If you reverse the chemical equation, you take the inverse of K
- Notice that the UNITS change
- In equilibrium problems, the units of K are often omitted (see tute for explanation)
Equilibria for coupled reactions

Consider the following sequential atmospheric reactions:

\[ \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \quad K_1 = 4.3 \times 10^{-25} \]

\[ 2\text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g) \quad K_2 = 6.4 \times 10^9 \]

We can add up these chemical reactions to provide an overall reaction:
### Form of Chemical Equation

<table>
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<tr>
<th>Form of Chemical Equation</th>
<th>Form of $Q$</th>
<th>Value of $K$</th>
</tr>
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<tr>
<td>Reference reaction: $A \rightleftharpoons B$</td>
<td>$Q_{(ref)} = \frac{[B]}{[A]}$</td>
<td>$K_{(ref)} = \frac{[B]<em>{eq}}{[A]</em>{eq}}$</td>
</tr>
<tr>
<td>Reverse reaction: $B \rightleftharpoons A$</td>
<td>$Q = \frac{1}{Q_{(ref)}} = \frac{[A]}{[B]}$</td>
<td>$K = \frac{1}{K_{(ref)}}$</td>
</tr>
<tr>
<td>Reaction as sum of two steps:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1) $A \rightleftharpoons C$</td>
<td>$Q_1 = \frac{[C]}{[A]}$; $Q_2 = \frac{[B]}{[C]}$</td>
<td>$K_{overall} = K_1 \times K_2$</td>
</tr>
<tr>
<td>(2) $C \rightleftharpoons B$</td>
<td>$Q_{overall} = Q_1 \times Q_2 = Q_{(ref)}$</td>
<td></td>
</tr>
<tr>
<td>Coefficients multiplied by $n$</td>
<td>$Q = Q_{(ref)}^n$</td>
<td>$K = K_{(ref)}^n$</td>
</tr>
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</table>
Different kinds of eq’m constant

So far we have used the symbol $K_{eq}$ or just $K$ to represent the equilibrium constant.

Sometimes we want to associate the eq’m constant with a particular type of reaction, or particular units. We then use a different subscript on the $K$ but really there is no difference to the way we treat the problem.

\[ e.g. \quad K_a = \text{acid dissociation eq’m constant}; \]
\[ K_b = \text{base dissociation eq’m constant}; \]
\[ K_w = \text{water dissociation eq’m constant}; \]
\[ K_p = \text{eq’m constant in units of pressure}; \]
\[ K_c = \text{eq’m constant specifically in concentration units}; \]
\[ K_{stab} = \text{eq’m constant for stability of a complex}; \]
\[ K_{sp} = \text{solubility product constant}. \]
Equilibria involving (l) and (s)

Consider the “water gas” reaction, which is used to make combustible gases from coal:

\[ C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \]

The equilibrium constant can be written as:

\[ K = \frac{[CO][H_2]}{[H_2O][C]} \]

But the “concentration”, i.e. mol/L, of C(s) is constant (the “concentration” of a solid is its density, which is independent of how much substance is present). Therefore this constant can be incorporated into the equilibrium constant:

\[ K' = \frac{[CO][H_2]}{[H_2O]} \]

In general: equilibrium constant expressions DO NOT contain concentration factors for pure solids or liquids.
Equilibria involving (l) and (s)

Consider two identical closed flasks containing different amounts of water at the same temperature:

\[ \text{H}_2\text{O (l)} \rightleftharpoons \text{H}_2\text{O (vap)} \]

Vapour pressure does not depend on how much liquid is present.

Consider the decomposition of mercuric oxide:

\[ 2\text{HgO (s)} \rightleftharpoons 2\text{Hg (l)} + \text{O}_2 (g) \]
Decomposition of calcium carbonate:

$$\text{CaCO}_3(s) \rightleftharpoons \text{CaO} \text{(s)} + \text{CO}_2 \text{(g)}$$

The equilibrium doesn't depend on the amount of solid, only on the amount of gas.

$$K_c = [\text{CO}_2]$$

$$K_p = p_{\text{CO}_2}$$
Example questions

CONCEPTS
- The equilibrium state
- The dynamic nature of eq’m (kinetic picture)
- The relationship between $\Delta H$ and eq’m
- How to write $K_{eq}$ for any reaction
- The reaction quotient

CALCULATIONS
- Work out $K_{eq}$ from eq’m concentrations
- Work out Q from any set of concentrations
- Work out whether a system is at eq’m
- Work out the direction of chemical change.