



Equilibrium

What is equilibrium?

Hebden – Unit 2
(page 37-69)

Dynamic Equilibrium

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Experiments show that most reactions, when carried out in a closed system, do **NOT** undergo complete conversion from reactants to products regardless of the time allowed for the reaction to take place.

Dynamic Equilibrium

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What happens is, products begin to react with each other to re-form the reactants. In time, a STEADY-STATE situation results such that

$$\text{Rate}_{\text{(formation of products)}} = \text{Rate}_{\text{(formation of reactants)}}$$

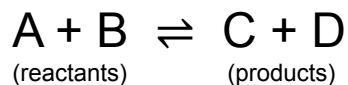
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Dynamic Equilibrium

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$$\text{Rate}_{\text{(formation of products)}} = \text{Rate}_{\text{(formation of reactants)}}$$



At this point, the concentrations of all the reactants and products remain constant.

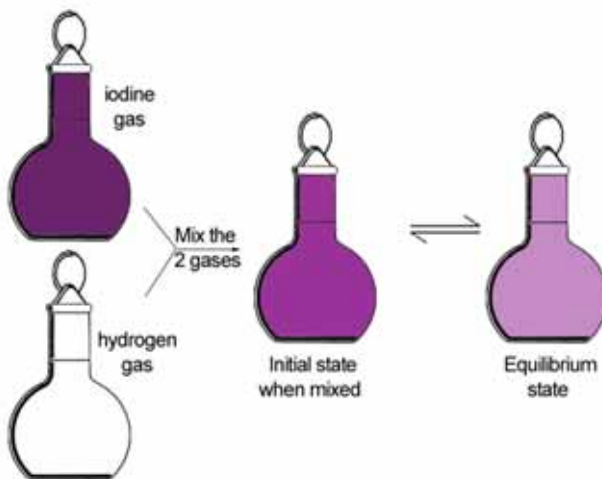
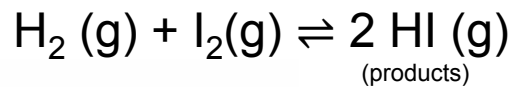
The reaction has reached **CHEMICAL EQUILIBRIUM**.

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After some time, equilibrium state is reached.

The colour of the vapour remains constant.

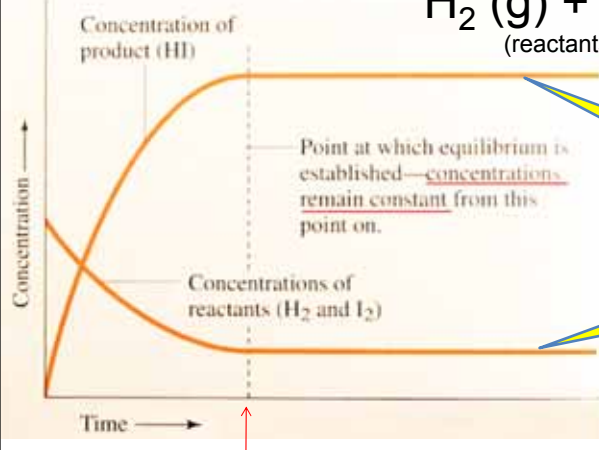
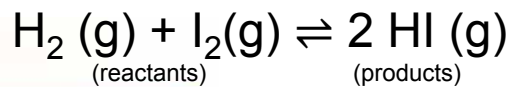
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Concentration VS. Time



Concentrations of HI remain constant.

Concentrations of H_2 and I_2 remain constant.

NOTE: Concentrations of reactants and products do NOT have to be equal.

The reaction is at **CHEMICAL EQUILIBRIUM**.

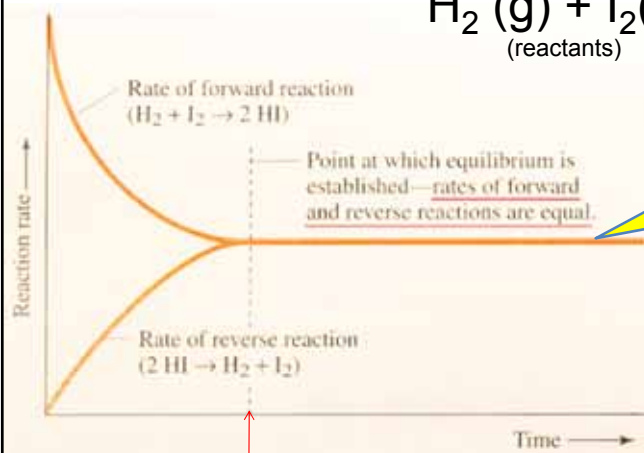
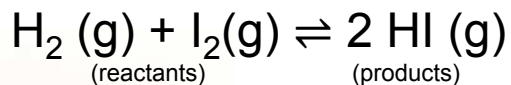
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Reaction Rate VS. Time



Forward and reverse
reaction rates are
EQUAL.

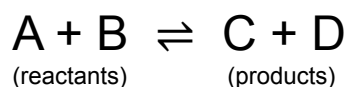
The reaction is at **CHEMICAL EQUILIBRIUM**.

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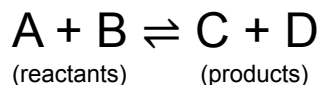
Chemical equilibrium is the process wherein two opposing chemical reactions occur simultaneously at the same rate.

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Characteristics of Equilibrium:

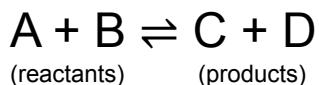
1. Forward rate = Reverse rate.
2. [Reactants] and the [Products] are constant.
3. In general, [Reactants] does not equal [Products].
4. Equilibrium is temperature dependent.
5. If an equilibrium is disturbed, it will re-establish itself.
6. A state of equilibrium can be established from any starting point.

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Three types of equilibrium:

1. Phase equilibrium - A substance undergoes phase changes
2. Solubility equilibrium – A solute interacts with a solvent
3. Chemical reaction equilibrium

For each of the above, we need to identify what is actually in equilibrium.

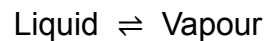
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1. Phase Equilibrium



Two process in opposition:

- Evaporation is the forward reaction.
- Condensation is the reverse reaction.

Rate of evaporation = Rate of condensation

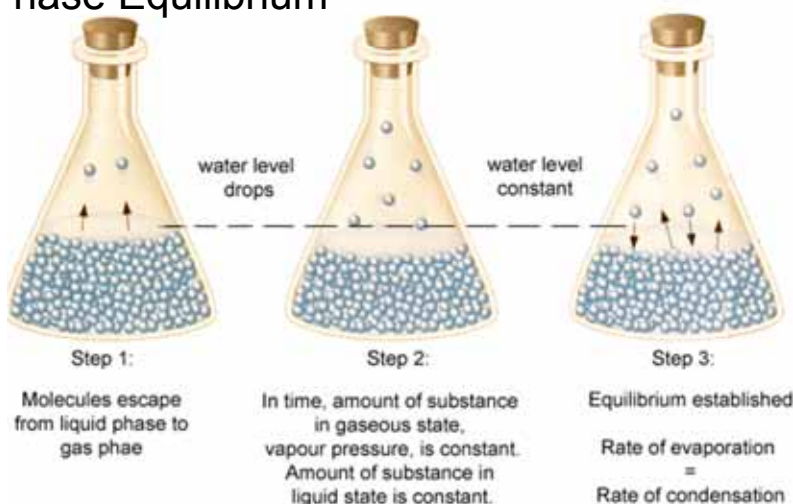
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1. Phase Equilibrium



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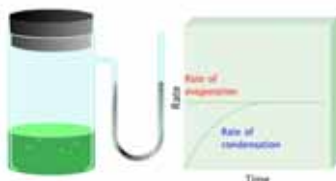
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1. Phase Equilibrium



- Evaporation is the forward reaction.
- Condensation is the reverse reaction.



Rate of evaporation = Rate of condensation

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2. Solubility Equilibrium



- Dissolution is the forward reaction.
- Crystallization is the reverse reaction.

The opposing processes are in dynamic equilibrium when the solution is saturated. That is, the solution is holding all the solute it can at a given temperature.

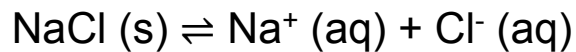
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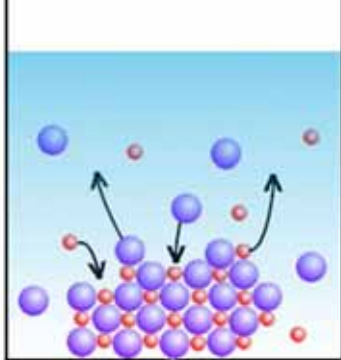
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2. Solubility Equilibrium



A saturated sodium chloride solution



A saturated solution has an established equilibrium between dissolved and un-dissolved particles.

Rate of dissolution = Rate of crystallization

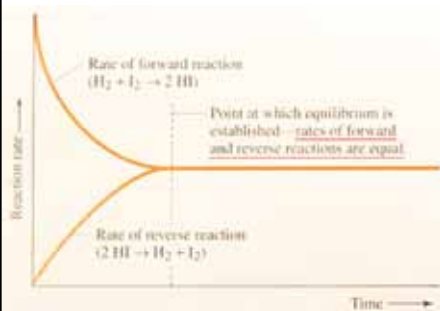
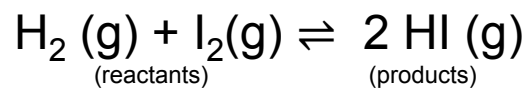
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3. Chemical Reaction Equilibrium



$\text{Rate}_{\text{(forward)}} = \text{Rate}_{\text{(reverse)}}$

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Dynamic Equilibrium

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Summary

A state of equilibrium can exist when:

1. There needs to be a closed system.
2. The reaction is REVERSIBLE.
3. No observable change in the *macroscopic* property (i.e. concentrations)
4. The temperature is constant

We will need to look for the macroscopic property.

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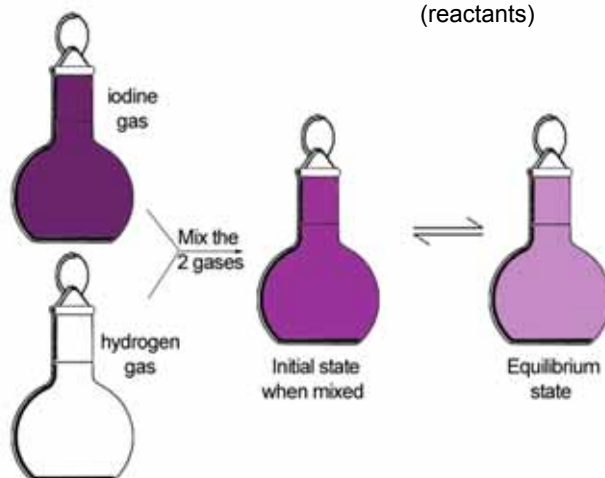
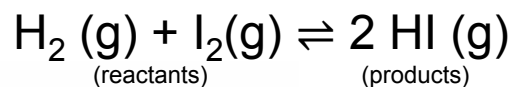
Equilibrium

Recognizing Equilibrium States

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Dynamic Equilibrium

Hebden – Unit 2 (page 37-69)



After some time,
equilibrium
state is
reached.

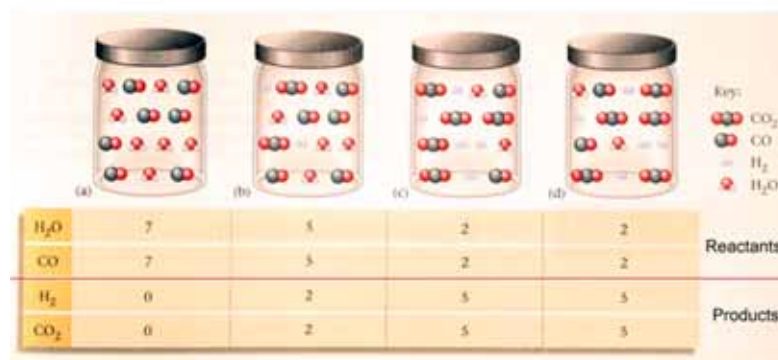
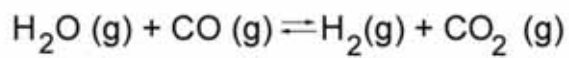
The colour of the vapour remains constant.

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Dynamic Equilibrium

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Start with
reactants
only

Reactants begin to be used up

Products begin to form

In time, more reactants are converted to products

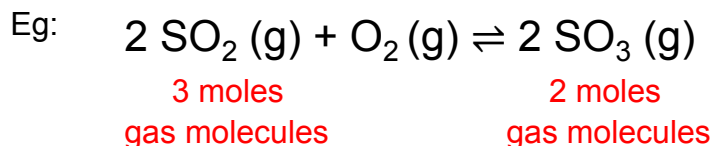
No more changes
in the amount
of reactants and
products.
Equilibrium
established!!!

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Dynamic Equilibrium

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We need to look for a property in the chemical reaction in order to determine whether a reaction is in a state of equilibrium.



Macroscopic property:

- Pressure ↓ in the forward reaction.
- Pressure ↑ in the reverse reaction.
- When equilibrium state is reached, the pressure of the system is constant.

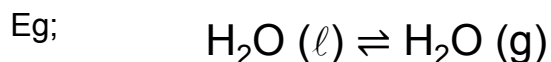
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Dynamic Equilibrium

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We need to look for a property in the chemical reaction in order to determine whether a reaction is in a state of equilibrium.



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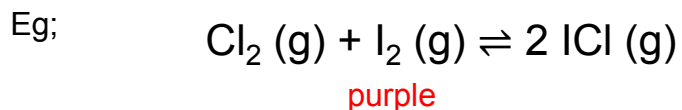
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Dynamic Equilibrium

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We need to look for a property in the chemical reaction in order to determine whether a reaction is in a state of equilibrium.



Macroscopic property:

- Colour ↓ in the forward reaction.
- Colour ↑ in the reverse reaction.
- When equilibrium state is reached, the colour of the system is constant.

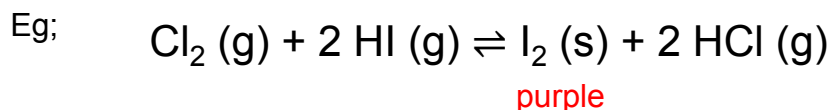
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Dynamic Equilibrium

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We need to look for a property in the chemical reaction in order to determine whether a reaction is in a state of equilibrium.



Macroscopic properties

First property

- Colour ↑ in the forward reaction.
- Colour ↓ in the reverse reaction.
- When equilibrium state is reached, the colour of the system is constant.

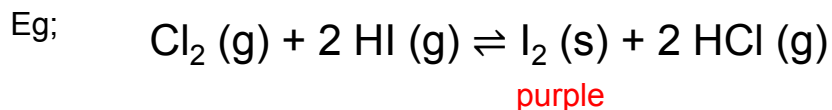
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Dynamic Equilibrium

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We need to look for a property in the chemical reaction in order to determine whether a reaction is in a state of equilibrium.



Macroscopic properties:

Second property

- Pressure ↓ in the forward reaction.
- Pressure ↑ in the reverse reaction.
- When equilibrium state is reached, the pressure of the system is constant.

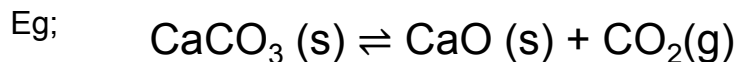
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Dynamic Equilibrium

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We need to look for a property in the chemical reaction in order to determine whether a reaction is in a state of equilibrium.



Macroscopic properties:

- Pressure ↑ in the forward reaction.
- Pressure ↓ in the reverse reaction.
- When equilibrium state is reached, the pressure of the system is constant.

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Equilibrium

Endothermic / Exothermic

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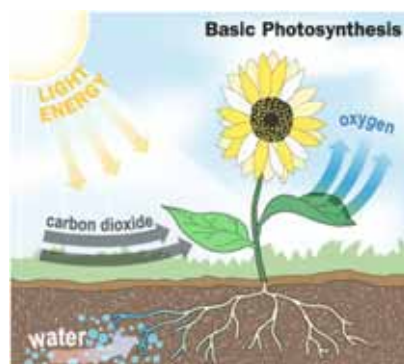
Dynamic Equilibrium

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Endothermic reaction: reactions requiring input of energy

Eg. – Photosynthesis –

Plants use the energy from the sun to convert CO_2 and water to glucose and oxygen.



Dynamic Equilibrium

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Endothermic reaction: reactions requiring input of energy

Eg. – Dissolving compounds in water:

- Ammonium chloride
- Ammonium nitrate
- Potassium chloride



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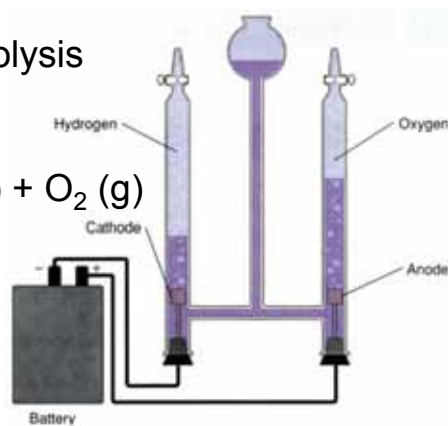
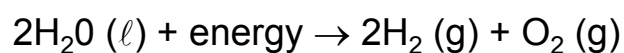
Dynamic Equilibrium

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Endothermic reaction: reactions requiring input of energy

Eg. - Melting ice

- Boiling water
- Splitting water - electrolysis



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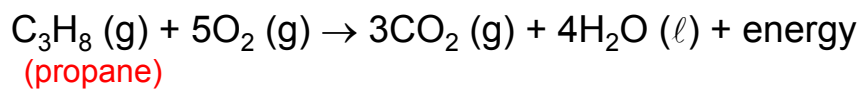
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Dynamic Equilibrium

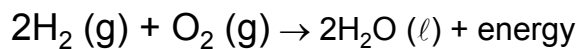
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Exothermic reaction: reactions produce energy

Eg. – Combustion reactions



Eg. – Synthesis of water from its elements



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Dynamic Equilibrium

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What determines whether
a chemical reaction is
ENDOTHERMIC or EXOTHERMIC?

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Dynamic Equilibrium

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The strength of the chemical bonds before and after the chemical reaction.

- When bonds are broken in the reactants, energy is required.
- When new bonds are formed as products, energy is released.

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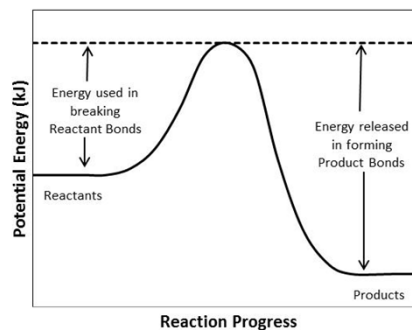
Dynamic Equilibrium

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The change in energy observed for a chemical reaction is called Enthalpy, H.

$$\Delta H = \begin{array}{c} \text{energy used in bond} \\ \text{breaking the reactants} \end{array} - \begin{array}{c} \text{energy released in bond} \\ \text{forming products} \end{array}$$

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$



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Dynamic Equilibrium

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The change in energy observed for a chemical reaction is called Enthalpy, H.

$$\Delta H = \frac{\text{energy used in bond breaking the reactants}}{\text{energy released in bond forming products}}$$

Endothermic reaction:

1. $\frac{\text{energy used in bond breaking the reactants}}{\text{energy released in bond forming products}} >$
2. $H_{\text{reactants}} < H_{\text{products}}$
3. $\Delta H = H_{\text{products}} - H_{\text{reactants}} > 0$

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Dynamic Equilibrium

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The change in energy observed for a chemical reaction is called Enthalpy, H.

$$\Delta H = \frac{\text{energy used in bond breaking the reactants}}{\text{energy released in bond forming products}}$$

Exothermic reaction:

1. $\frac{\text{energy used in bond breaking the reactants}}{\text{energy released in bond forming products}} <$
2. $H_{\text{reactants}} > H_{\text{products}}$
3. $\Delta H = H_{\text{products}} - H_{\text{reactants}} < 0$

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Dynamic Equilibrium

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Let's take a look at the reaction profiles of endothermic and exothermic reactions.

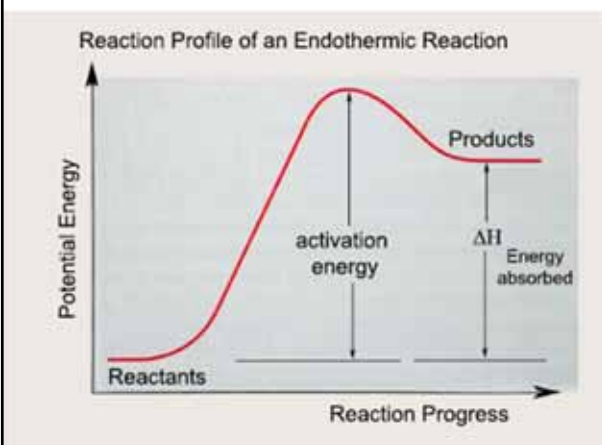
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Dynamic Equilibrium

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Endothermic reaction:



$$H_{\text{products}} > H_{\text{reactants}}$$

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

$$\Delta H > 0$$

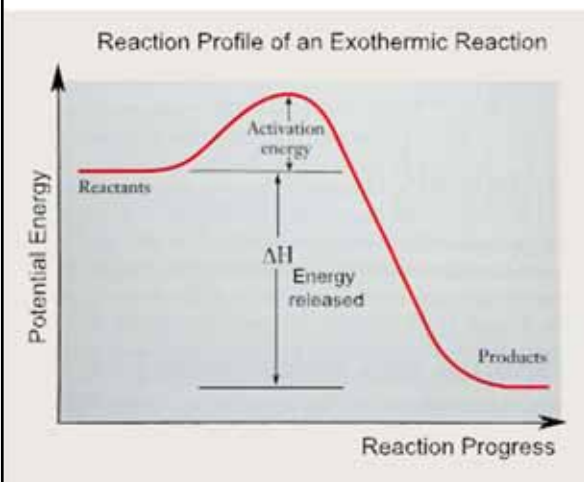
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Dynamic Equilibrium

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Exothermic reaction:



$$H_{\text{products}} < H_{\text{reactants}}$$

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

$$\Delta H < 0$$

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Dynamic Equilibrium

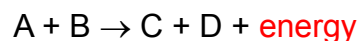
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To include *energy* in the chemical reaction,

Endothermic reaction: heat in; energy on the reactant side.
Heat **Ent**ers the reaction. **En**dothermic.



Exothermic reaction: heat produced; energy on the product side.
Heat **Ex**its the reaction, **Ex**othermic.



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Equilibrium

Factors Controlling Equilibrium

Enthalpy and Entropy

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Dynamic Equilibrium

Hebden – Unit 2 (page 37-69)

Factors Controlling Equilibrium

Two driving factors (or tendencies) must be considered for all chemical reactions:

1. Enthalpy
2. Entropy

Dynamic Equilibrium

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1. Enthalpy

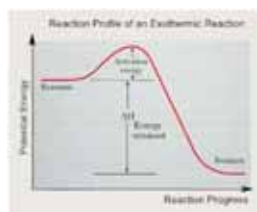
The tendency is to achieve an overall **LOWER** enthalpy.

Endothermic



Uphill in energy
NOT PREFERRED

Exothermic



Downhill in energy
PREFERRED

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Dynamic Equilibrium

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1. Enthalpy

The tendency is to achieve an overall **LOWER** enthalpy.

For an **endothermic** reaction:



Uphill in energy
NOT PREFERRED

- Reactants have LOWER energy than the products.
- The drive is towards the formation of reactants (the state of lower enthalpy)

Therefore, reactant formation
is favoured because it is
downhill in energy.

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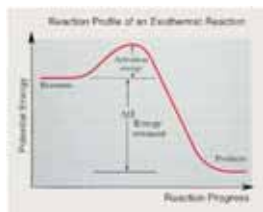
Dynamic Equilibrium

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1. Enthalpy

The tendency is to achieve an overall **LOWER** enthalpy.

For an **exothermic** reaction:



- Products have **LOWER** energy than the reactants.
- The drive is towards the formation of products (the state of lower enthalpy)

Downhill in energy
PREFERRED

Therefore product formation
is favoured because it is
downhill in energy.

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Dynamic Equilibrium

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2. Entropy

- Entropy is a measure of randomness or disorder.
- Qualitatively, we can approximate entropy.

Gases > Solutions > Liquids > Solids
(higher entropy) (lower entropy)

- The tendency is to achieve a **HIGHER** state of disorder or randomness.

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Dynamic Equilibrium

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2. Entropy

- In a chemical reaction,
 - if entropy is increased, product formation is favoured.
 - If entropy is decreased, reactant formation is favoured.
- $\Delta S = S_{\text{products}} - S_{\text{reactants}}$
- If $\Delta S > 0$, products have HIGHER entropy than reactants.
{disorder}
{randomness}
- If $\Delta S < 0$, products have LOWER entropy than reactants.
{disorder}
{randomness}

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Dynamic Equilibrium

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2. Entropy

- The greater the degree of randomness or disorder in a system, the greater the entropy of the system
- Entropy increases are expected to accompany processes in which
 - Pure liquids or liquids solutions are formed from solids
 - Gases are formed, either from solids or liquids
 - The number of molecules of gases increase during the reaction
 - The temperature of a substance is increased (increased temperature means increased molecular motion)

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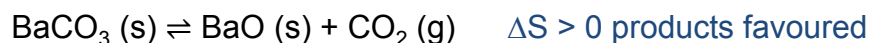
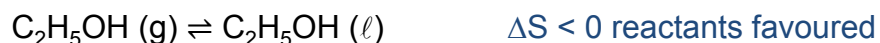
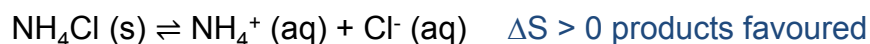
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Dynamic Equilibrium

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2. Entropy

Predict ΔS for the following reactions:



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Dynamic Equilibrium

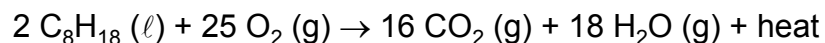
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Putting it together and take a look at BOTH enthalpy and entropy at work.

Case I: When BOTH enthalpy and entropy FAVOUR products.

- It means $\Delta H < 0$ (exothermic) and $\Delta S > 0$
- Reaction can go to COMPLETION
- Reaction is SPONTANEOUS

Eg – Combustion of octane is spontaneous



Heat is produced. $\Delta H < 0$ exothermic[↗]

25 gas molecules \rightarrow 34 gas molecules $\Delta S > 0$

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Dynamic Equilibrium

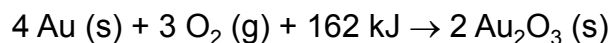
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Putting it together and take a look at BOTH enthalpy and entropy at work.

Case II: When BOTH enthalpy and entropy FAVOUR reactants.

- It means $\Delta H > 0$ (endothermic) and $\Delta S < 0$
- Reaction will not go. No reaction.
- Reaction will not occur spontaneously.

Eg –



Heat is required. $\Delta H > 0$ endothermic

3 gas molecules \rightarrow no gas molecules $\Delta S < 0$

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Dynamic Equilibrium

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Putting it together and take a look at BOTH enthalpy and entropy at work.

Case III: When enthalpy and entropy FAVOUR opposing sides (i.e. one favours products, the other favours reactants).

- $\Delta H < 0$ (exothermic, favours products) and $\Delta S < 0$ favours reactants
- $\Delta H > 0$ (endothermic, favours reactants) and $\Delta S > 0$ favours products
- Reactions form **EQUILIBRIUM** which can shift in the forward and reverse direction.

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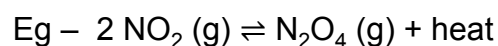
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Dynamic Equilibrium

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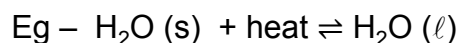
Putting it together and take a look at BOTH enthalpy and entropy at work.

Case III (cont'd): When enthalpy and entropy FAVOUR opposing sides (i.e. one favours products, the other favours reactants).



$\Delta H < 0$ exothermic; products favoured

$\Delta S < 0$ entropy favors reactants



$\Delta H > 0$ endothermic; reactants favoured

$\Delta S > 0$ entropy favors products

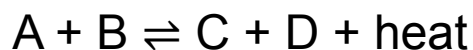


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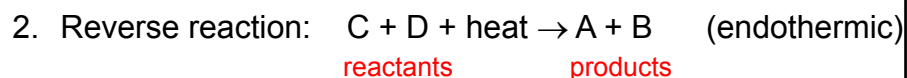
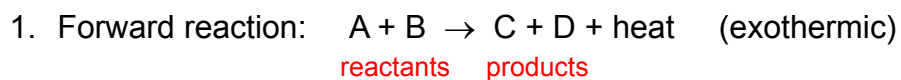
Dynamic Equilibrium

Hebden – Unit 2 (page 37-69)

Let's take a look at the reaction profiles for reversible reactions.



Write it separately,



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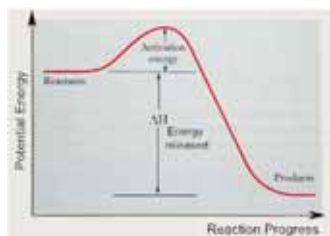
54

Dynamic Equilibrium

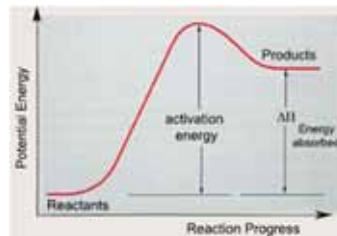
Hebden – Unit 2 (page 37-69)



Forward reaction



Reverse reaction



- Points to note:
- E_a (forward) < E_a (reverse)
 - $\Delta H_{\text{forward}} < 0$ - exothermic
 - $\Delta H_{\text{reverse}} > 0$ - endothermic

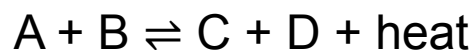
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Dynamic Equilibrium

Hebden – Unit 2 (page 37-69)

It is important to understand the factors that control the **position** of a chemical equilibrium.



Example: Industrial chemical manufacturers

The chemical engineers in charge of production **WANT** to choose conditions that **FAVOUR** formation of products.



What conditions can be changed to effectively cause the position of the equilibrium to lie as far to the right as possible?

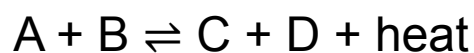
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Dynamic Equilibrium

Hebden – Unit 2 (page 37-69)

It is important to understand the factors that control the **position** of a chemical equilibrium.



Let's take a look at the effects on the position of a chemical equilibrium when the following conditions are changed:

1. Concentration
2. Temperature
3. Pressure
4. Volume

It turns out that we can **predict** how these conditions have on a system at equilibrium!

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Equilibrium

Le Chatelier's Principle

Hebden – Unit 2
(page 37-69)

Le Chatelier's Principle

Hebden – Unit 2 (page 50-55)

We can use **Le Chatelier's Principle** to qualitatively predict the effects of changes by:

1. Changing concentration
2. Changing temperature
3. Adding an inert gas
4. Changing the pressure
5. Changing the volume

on a system at equilibrium.

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Le Chatelier's Principle

Hebden – Unit 2 (page 50-55)

Le Chatelier's Principle

When a stress is applied to a closed system at equilibrium, the system will respond to **REDUCE** the stress and establish a new equilibrium.



Photo from Wiki

Henri Louis Le Chatelier, a French/Italian chemist and engineer.

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Le Chatelier's Principle

Hebden – Unit 2 (page 50-55)

Le Chatelier's Principle

When a stress is applied to a closed system at equilibrium, the system will respond to REDUCE the stress and establish a new equilibrium.

Macroscopically, as a consequence of the stress on the equilibrium, we observe **SHIFTS** in the equilibrium in the **FORWARD** or **REVERSE** direction. We will call the observable as a “shift to the RIGHT” (forward) or a “shift to the LEFT” (reverse).

Physically, we observe the shift by seeing a visible colour change, a pressure change, etc...

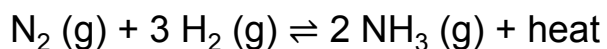
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Le Chatelier's Principle – Effect of Concentration Change

Hebden – Unit 2 (page 50-55)

Let's examine the equilibrium reaction of



At $t = 0$ min, the initial concentrations are:

$[\text{H}_2] = 2.400 \text{ M}$,
 $[\text{N}_2] = 0.800 \text{ M}$
 $([\text{NH}_3] = 0.000 \text{ M})$



Let's keep the equilibrium reaction at constant temperature.

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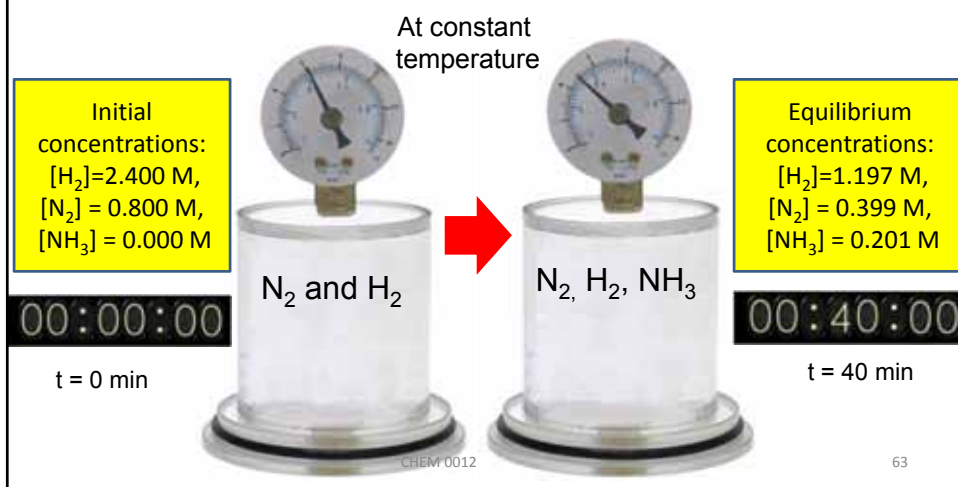
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Le Chatelier's Principle – Effect of Concentration Change

Hebden – Unit 2 (page 50-55)

Let's examine the equilibrium reaction of

$$\text{N}_2 (\text{g}) + 3 \text{H}_2 (\text{g}) \rightleftharpoons 2 \text{NH}_3 (\text{g}) + \text{heat}$$



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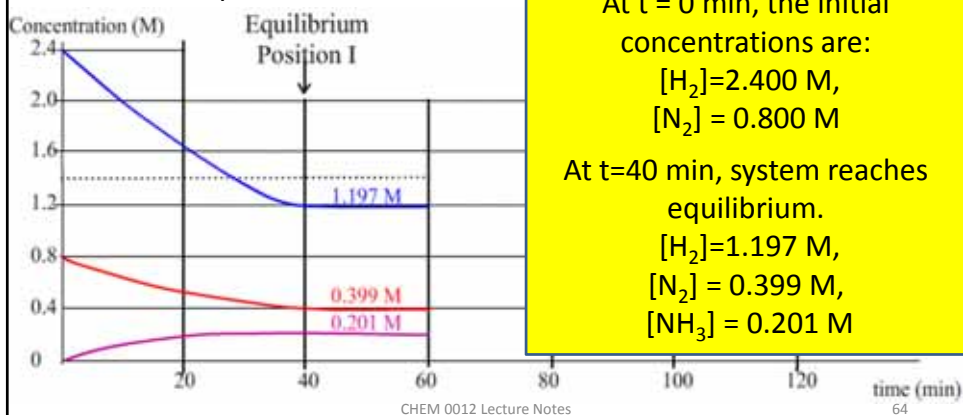
Le Chatelier's Principle – Effect of Concentration Change

Hebden – Unit 2 (page 50-55)

Let's examine the "Concentration VS. Time" graph for

$$\text{N}_2 (\text{g}) + 3 \text{H}_2 (\text{g}) \rightleftharpoons 2 \text{NH}_3 (\text{g}) + \text{heat}$$

At constant temperature,

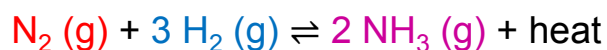


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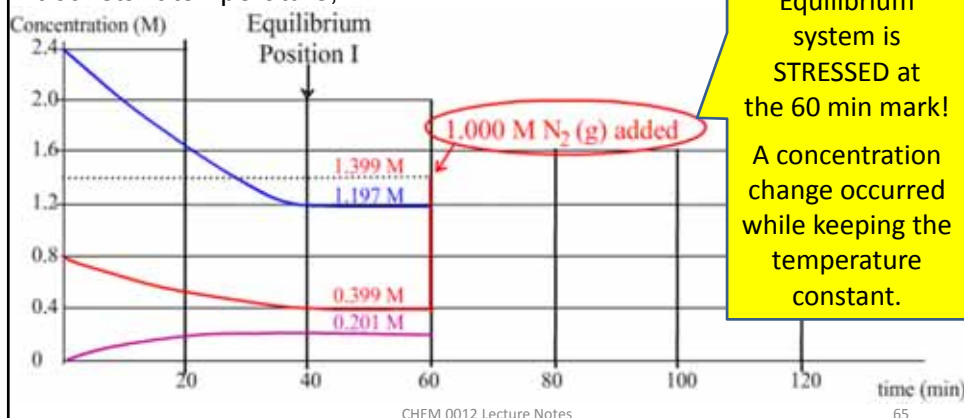
Le Chatelier's Principle – Effect of Concentration Change

Hebden – Unit 2 (page 50-55)

Let's examine the "Concentration VS. Time" graph for



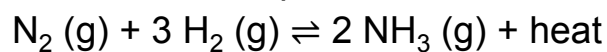
At constant temperature,



Le Chatelier's Principle – Effect of Concentration Change

Hebden – Unit 2 (page 50-55)

Let's examine the equilibrium reaction of



Equilibrium concentrations achieved:

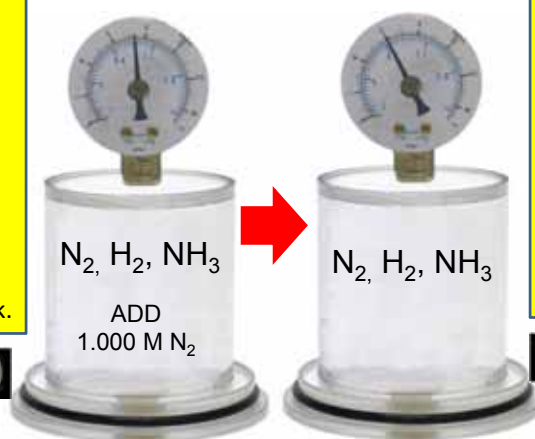
[H₂] = 1.197 M,
[N₂] = 0.399 M,
[NH₃] = 0.201 M

STRESS

EQUILIBRIUM

ADD 1.000 M N₂ at the 60 min mark.

01:00:00



40 minutes later, a new equilibrium re-establishes!

New equilibrium concentrations:

[H₂] = 1.044 M,
[N₂] = 1.348 M,
[NH₃] = 0.304 M

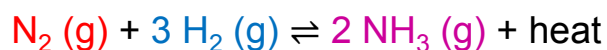
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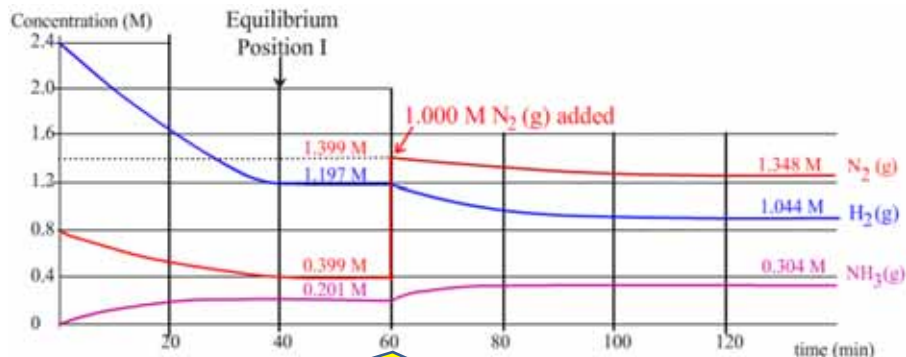
Le Chatelier's Principle – Effect of Concentration Change

Hebden – Unit 2 (page 50-55)

Let's examine the "Concentration VS. Time" graph for



At constant temperature,



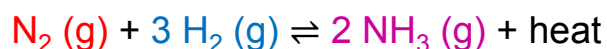
System responds to **REDUCE** the stress!

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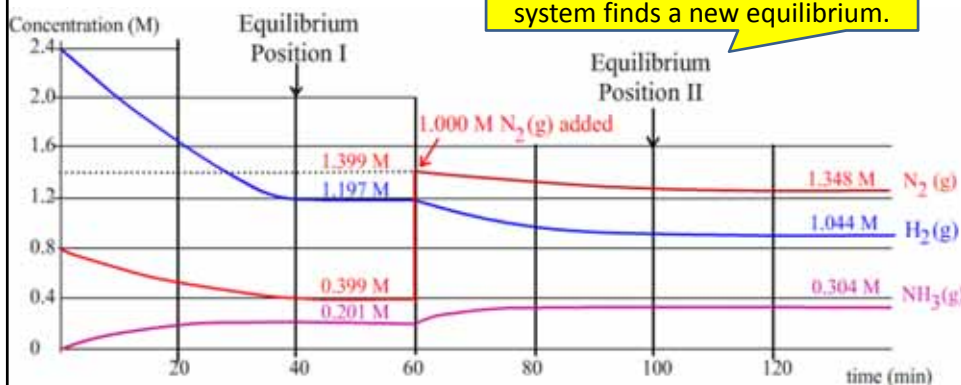
Le Chatelier's Principle – Effect of Concentration Change

Hebden – Unit 2 (page 50-55)

Let's examine the "Concentration VS. Time" graph for



At constant temperature,

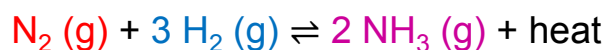


40 minutes after the stress, the system finds a new equilibrium.

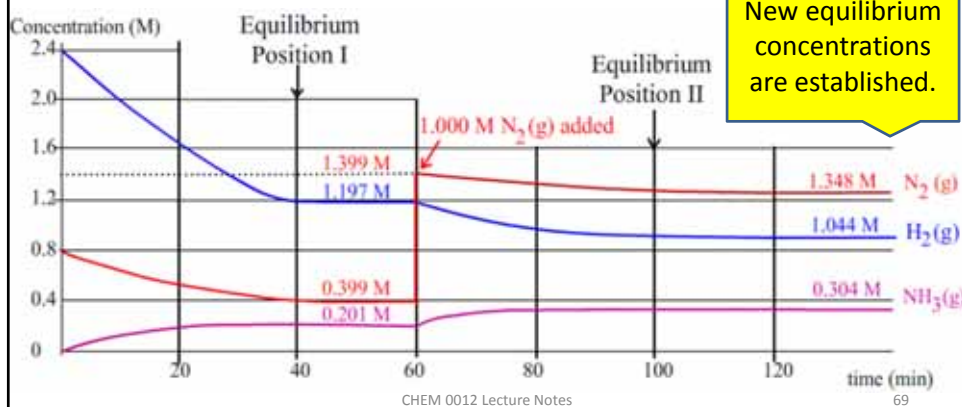
Le Chatelier's Principle – Effect of Concentration Change

Hebden – Unit 2 (page 50-55)

Let's examine the "Concentration VS. Time" graph for



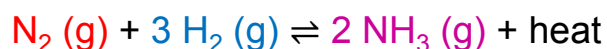
At constant temperature,



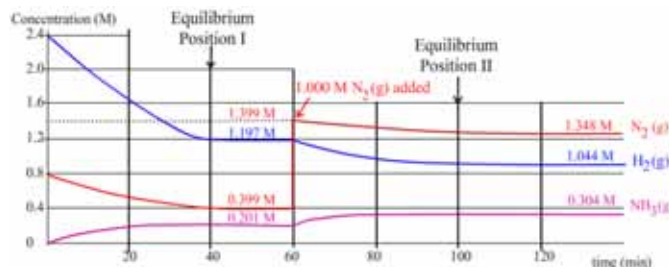
Le Chatelier's Principle – Effect of Concentration Change

Hebden – Unit 2 (page 50-55)

Let's examine the "Concentration VS. Time" graph for



At constant temperature,

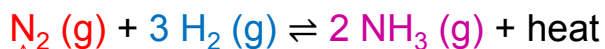


Now that we know how the system reacts to the stress. Let's understand this behaviour.

Le Chatelier's Principle – Effect of Concentration Change

Hebden – Unit 2 (page 50-55)

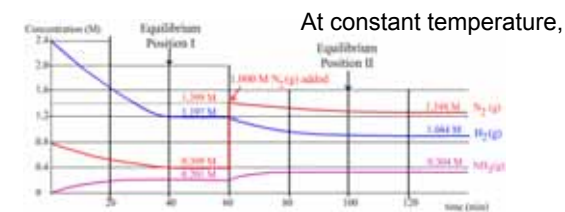
Let's examine the "Concentration VS. Time" graph for



Equilibrium was stressed by the addition of 1.000 M $\text{N}_2 (\text{g})$.

Le Chatelier's Principle says "... the system will respond to **REDUCE** the stress and establish a new equilibrium."

The system responds by **reducing** the amount of N_2 added.
The equilibrium responds by shifting to the **RIGHT** to remove the added N_2 .



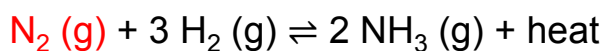
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Le Chatelier's Principle – Effect of Concentration Change

Hebden – Unit 2 (page 50-55)

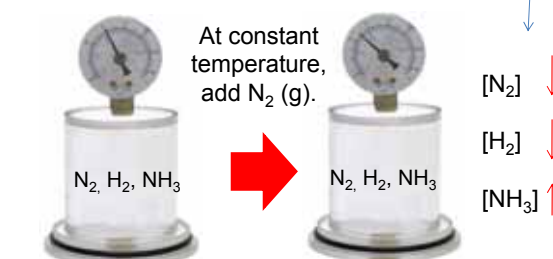
Summarize:



Equilibrium is stressed by the addition of N_2 .

Le Chatelier's Principle says "... the system will respond to **REDUCE** the stress and establish a new equilibrium."

The system responds by **reducing** the amount of N_2 added.
The equilibrium responds by shifting to the **RIGHT** to remove the added N_2 .



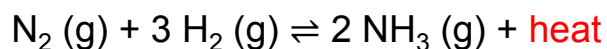
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Le Chatelier's Principle – Effect of Temperature Change

Hebden – Unit 2 (page 50-55)

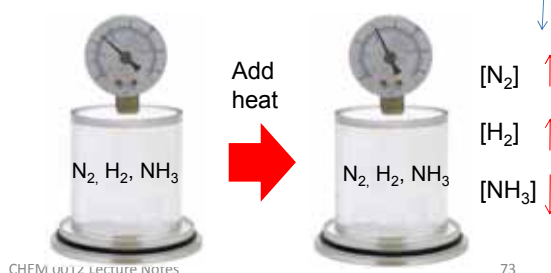
Let's examine the **exothermic** equilibrium reaction



Equilibrium is stressed by the addition of heat.

Le Chatelier's Principle says "... the system will respond to **REDUCE** the stress and establish a new equilibrium."

The system responds by **reducing** the amount of heat added. The exothermic equilibrium reaction responds by shifting to the **LEFT** to remove the added heat.



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Le Chatelier's Principle – Effect of Temperature Change

Hebden – Unit 2 (page 50-55)

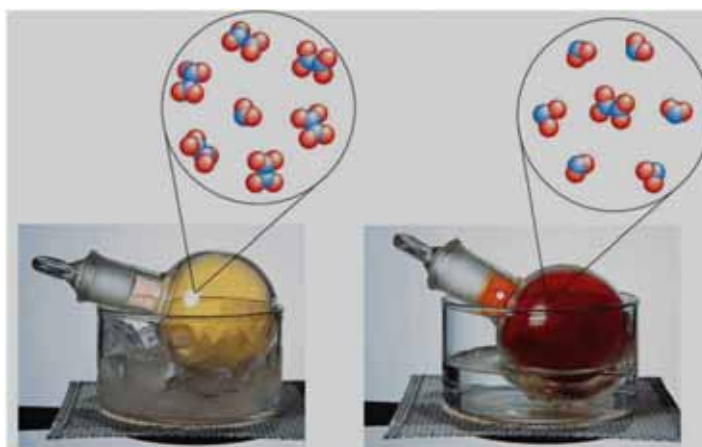
Let's examine the **endothermic** equilibrium reaction



Colourless

Red-brown

0°C



100°C

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Le Chatelier's Principle – Effect of Pressure Change

Hebden – Unit 2 (page 50-55)

What happens if the equilibrium is stressed by a change in pressure?

- The greatest effects will be on gaseous substances.
- Let's examine the ways to change the pressure of a reaction system that involves gaseous components:
 1. Add a gaseous product or reactant.
 2. Remove a gaseous product or reactant.
 3. Add an inert gas*
 - a) while holding the volume constant
 - b) while holding the pressure constant

* An inert gas is a gas that does not take part in the reaction.

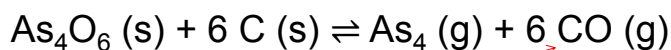
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Le Chatelier's Principle – Effect of Pressure Change

Hebden – Unit 2 (page 50-55)

1. Predict what would happen to the following equilibrium if CO (g) is added while the volume and the temperature are held constant.



Equilibrium is stressed by adding CO(g) (i.e. pressure increased).

Le Chatelier's Principle says "... the system will respond to **REDUCE** the stress and establish a new equilibrium."

The system responds by **reducing** the pressure of the system. The equilibrium reaction responds by shifting to the LEFT, the side to remove some of the CO(g).

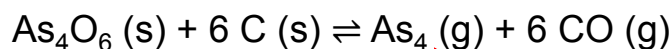
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Le Chatelier's Principle – Effect of Pressure Change

Hebden – Unit 2 (page 50-55)

2. Predict what would happen to the following equilibrium if $\text{As}_4(\text{g})$ is removed while the volume and the temperature are held constant.



Equilibrium is stressed by removing $\text{As}_4(\text{g})$ (i.e. pressure decreased).

Le Chatelier's Principle says "... the system will respond to **REDUCE** the stress and establish a new equilibrium."

The system responds by **increasing** the pressure of the system. The equilibrium reaction responds by shifting to the RIGHT, to produce more $\text{As}_4(\text{g})$.

* This reaction is used in the industrial extraction of Arsenic. As is continuously removed from the reaction system to increase the yield.

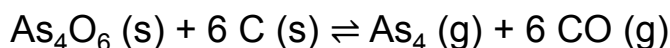
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Le Chatelier's Principle – Effect of Pressure Change

Hebden – Unit 2 (page 50-55)

- 3(a). Predict what would happen to the following equilibrium if $\text{He}(\text{g})$, an inert gas, is added while the volume and temperature are held constant.



Addition of $\text{He}(\text{g})$, an inert gas, to the system without changing the system's volume.

Addition of He gas increase the TOTAL pressure of the system. it has NO effect on the concentrations of the reactants and products.

$$p_{\text{CO}} = \frac{n_{\text{CO}}RT}{V} \quad p_{\text{As}_4} = \frac{n_{\text{As}_4}RT}{V}$$

Partial pressures of CO and As_4

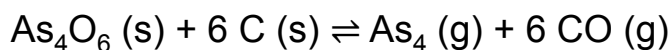
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No shift because the partial pressures of the gases are unchanged because volume is unchanged.

Le Chatelier's Principle – Effect of Pressure Change

Hebden – Unit 2 (page 50-55)

3 (b). Predict what would happen to the following equilibrium if He (g), an inert gas, is added while the pressure and temperature are held constant.



Equilibrium is stressed by the addition of He (g), an inert gas.

Le Chatelier's Principle says "... the system will respond to **REDUCE** the stress and establish a new equilibrium."

$$p_{\text{CO}} = \frac{n_{\text{CO}}RT}{V} \quad p_{\text{As}_4} = \frac{n_{\text{As}_4}RT}{V}$$

Partial pressures of CO and As₄

The system's volume **INCREASES** in order to maintain constant pressure. This results in a **DECREASE** the partial pressures (or concentration) of As₄ and CO.

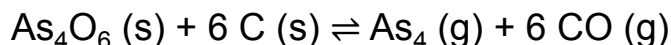
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As p_{CO} and p_{As_4} decrease, equilibrium will shift to the **RIGHT**, to increase the pressure of the system.

Le Chatelier's Principle – Effect of Volume Change

Hebden – Unit 2 (page 50-55)

Predict what would happen to the following equilibrium if the system's **volume is decreased** while temperature is constant.



Equilibrium is stressed because this will result in an increase in the system's pressure.

Le Chatelier's Principle says "... the system will respond to **REDUCE** the stress and establish a new equilibrium."

$$p_{\text{CO}} = \frac{n_{\text{CO}}RT}{V} \quad p_{\text{As}_4} = \frac{n_{\text{As}_4}RT}{V}$$

Partial pressures of CO and As₄

The **DECREASE** in the system's volume causes an increase in the partial pressures (or concentration) of As₄ and CO.

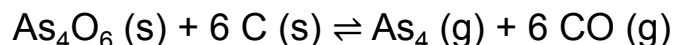
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As p_{CO} and p_{As_4} is increased, the equilibrium will shift to the **LEFT** to remove some CO (g) and As₄ (g).

Le Chatelier's Principle – Effect of Volume Change

Hebden – Unit 2 (page 50-55)

Predict what would happen to the following equilibrium if the system's **volume is increased** while temperature is constant.



Equilibrium is stressed because this will result in a decrease in the system's pressure.

Le Chatelier's Principle says "... the system will respond to **REDUCE** the stress and establish a new equilibrium."

$$p_{\text{CO}} = \frac{n_{\text{CO}}RT}{V} \quad p_{\text{As}_4} = \frac{n_{\text{As}_4}RT}{V}$$

Partial pressures of CO and As₄

The INCREASE in the system's volume causes a decrease in the partial pressures (or concentration) of As₄ and CO.

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As p_{CO} and p_{As_4} is decreased, the equilibrium will shift to the RIGHT to produce more CO (g) and As₄ (g).

Le Chatelier's Principle

Hebden – Unit 2 (page 50-55)

We have seen how to use **Le Chatelier's Principle** to qualitatively predict the effects of changes by:

1. Changing concentration
2. Changing temperature
3. Adding an inert gas
 - a) Changing the pressure
 - b) Changing the volume

on a system at equilibrium.

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Le Chatelier's Principle

Hebden – Unit 2 (page 50-55)

Le Chatelier's Principle

When a stress is applied to a closed system at equilibrium, the system will respond to **REDUCE** the stress and establish a new equilibrium.

We can predict the shift in equilibrium position as a result of the stress applied.

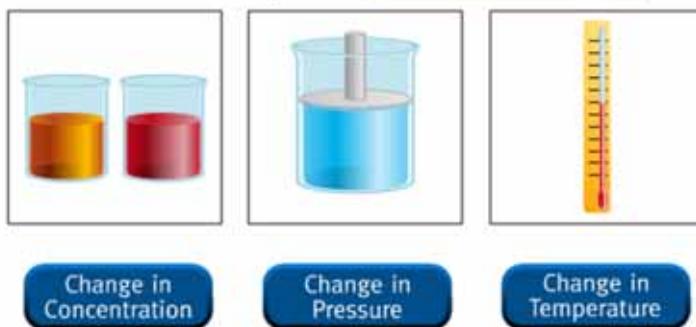
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Le Chatelier's Principle

Hebden – Unit 2 (page 50-55)

Le Chatelier's Principle – [View Animation](#)



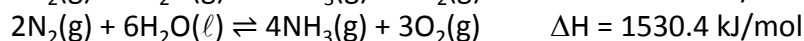
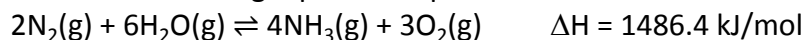
We can predict the shift in equilibrium position as a result of the stress applied.

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Le Châtelier's Principle Example

Consider the following equilibrium processes:

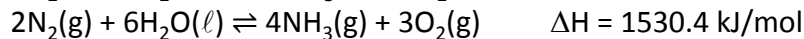
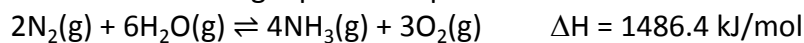


Indicate the effect on the mass of NH_3 and the value of K by:

Action taken	$\text{H}_2\text{O}(\text{g})$ m_{NH_3}	$\text{H}_2\text{O}(\ell)$ m_{NH_3}
Some N_2 removed		
Some H_2O added		
Volume increased		
Temperature decreased		
A catalyst is added		
Argon gas is added at constant volume		

Le Châtelier's Principle Example

Consider the following equilibrium processes:



Indicate the effect on the mass of NH_3 and the value of K by:

Action taken	$\text{H}_2\text{O}(\text{g})$ m_{NH_3}	$\text{H}_2\text{O}(\ell)$ m_{NH_3}
Some N_2 removed	↓	↓
Some H_2O added	↑	NC
Volume increased	↓	↑
Temperature decreased	↓	↓
A catalyst is added	NC	NC
Argon gas is added at constant volume	NC	NC



Equilibrium

Equilibrium Constant Expression and
the Equilibrium Constant, K_{eq}

Hebden – Unit 2
(page 37-69)

Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

1. Equilibrium Constant Expression
2. Equilibrium Constant, K_{eq}
3. K_c and K_p
4. Heterogeneous equilibrium
5. Equilibrium laws for
 - Combined equilibrium
 - Scaled equilibrium
 - Reversed equilibrium
6. Interpreting K_{eq} values
7. Explain Le Chatelier's Principle mathematically with K_{eq} .

Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

1. Equilibrium Constant Expression

- is a mathematical relationship that is specific for the equilibrium reaction

2. Equilibrium Constant, K_{eq}

- is a number that characterizes the equilibrium of the reaction
- is specific for the equilibrium reaction
- is temperature dependent

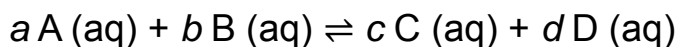
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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

For a general equilibrium reaction



where A and B are reactants,

C and D are products,

a , b , c , and d are the coefficients in the balanced chemical equilibrium.

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

Equilibrium
expression

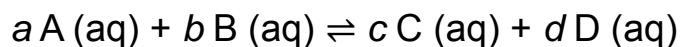
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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

For a general equilibrium reaction



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

Where does the equilibrium expression come from?

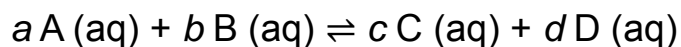
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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

For a general equilibrium reaction



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

Definition of
equilibrium!

$$\text{Rate}_{(\text{forward reaction})} = \text{Rate}_{(\text{reverse reaction})}$$

$$\text{Rate}_{(\text{forward reaction})} = k_{\text{forward}} [A]^a [B]^b$$

$$\text{Rate}_{(\text{reverse reaction})} = k_{\text{reverse}} [C]^c [D]^d$$

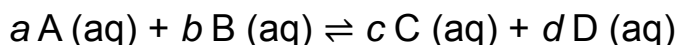
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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

For a general equilibrium reaction



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

Rate_(forward reaction) = **Rate**_(reverse reaction)

$$k_{\text{forward}} [A]^a [B]^b = k_{\text{reverse}} [C]^c [D]^d$$

$$K_{eq} = \frac{k_{\text{forward}}}{k_{\text{reverse}}} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

$$K_{eq} = \frac{[\text{Products}]}{[\text{Reactants}]}$$

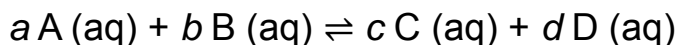
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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

For a general equilibrium reaction



Points to note about the Equilibrium Constant Expression:

- $[A]$, $[B]$, $[C]$, $[D]$ that is used in the Equilibrium Constant Expression must be **the equilibrium concentrations of A, B, C, and D**.
- For aqueous ions in solutions, the concentration unit is moles/L.

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

K_{eq} is
unitless.

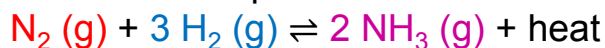
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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

Let's re-examine the equilibrium



The equilibrium constant expression is

$$K_{eq} = \frac{[\text{NH}_3]^2}{[\text{N}_2] \cdot [\text{H}_2]^3}$$

If we use molar concentrations for $[\text{N}_2]$, $[\text{H}_2]$ and $[\text{NH}_3]$, then

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2] \cdot [\text{H}_2]^3}$$

K_c is
unitless.

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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

For gaseous systems, we can express concentration of the gas in terms of **partial pressure of gases** rather than molar concentrations.

Assuming ideal gas behaviour,

$$PV = nRT$$

where P = pressure of the gas
 V = volume of the gas
 n = number of moles of the gas
 R = gas constant,
 T = temperature in Kelvin

Rearrange,

$$P = \frac{nRT}{V}$$

At constant temperature,

$$P \propto \frac{n}{V}$$

pressure is directly proportional
to the concentration of the gas.

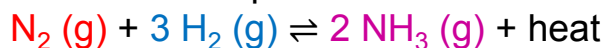
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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

Let's re-examine the equilibrium



The equilibrium constant expression, $K_{eq} = \frac{[\text{NH}_3]^2}{[\text{N}_2] \cdot [\text{H}_2]^3}$,

can also be calculated using partial pressures of the gases.

$$K_p = \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} \cdot p_{\text{H}_2}^3}$$

where p_{NH_3} , p_{N_2} , p_{H_2}
are partial pressures of
 NH_3 , N_2 , and H_2 in units of atm.

K_p is
unitless

$$\left(p_{\text{NH}_3} = \frac{n_{\text{NH}_3} RT}{V} \quad p_{\text{N}_2} = \frac{n_{\text{N}_2} RT}{V} \quad p_{\text{H}_2} = \frac{n_{\text{H}_2} RT}{V} \right)$$

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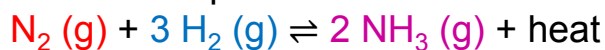
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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

3. K_c and K_p

Let's re-examine the equilibrium



$$K_p = \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} \cdot p_{\text{H}_2}^3}$$

(Concentrations in atm.)

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2] \cdot [\text{H}_2]^3}$$

(Concentrations in M.)

Both of these expressions give K_{eq} .

Are K_p and K_c equal?

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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

Are K_p and K_c equal?

For some reactions, K_p and K_c are equal. For others, the constants have DIFFERENT values.

$$K_p = K_c \cdot (RT)^{\Delta n_g}$$

Where R = gas constant = $0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$

T = temperature in Kelvin

$$\Delta n_g = n_{\text{products}} - n_{\text{reactants}}$$

(moles of gaseous products – moles of gaseous reactants)

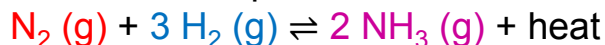
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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

Let's re-examine the equilibrium



$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2] \cdot [\text{H}_2]^3} = 6.0 \times 10^{-2} \quad \text{at } 500^\circ \text{C}$$

Convert to K_p :

$$\Delta n_g = n_{\text{products}} - n_{\text{reactants}} = 2 - 4 = -2$$

$$\begin{aligned} K_p &= K_c \cdot (RT)^{\Delta n_g} = 6.0 \times 10^{-2} (0.0821 \cdot 773)^{-2} \\ &= 1.5 \times 10^{-5} \end{aligned}$$

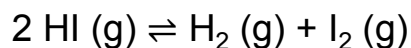
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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

Let's consider the equilibrium



$$\Delta n_g = n_{\text{products}} - n_{\text{reactants}} = 2 - 2 = 0$$

$$K_p = K_c \cdot (RT)^{\Delta n_g} = K_c (RT)^0 = K_c$$

In this case, $K_p = K_c$.

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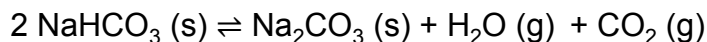
Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

4. Heterogeneous Equilibrium

- Equilibrium reaction has more than one phase
- Equilibrium reactions involving solids and liquids are **omitted** from the equilibrium constant expression because they have FIXED concentrations.

Example: The thermal decomposition of sodium bicarbonate



Since $\text{NaHCO}_3 \text{(s)}$ and $\text{Na}_2\text{CO}_3 \text{(s)}$ are solids, their concentrations are unchanged at a given temperature.

$$K_c = [\text{H}_2\text{O}] \cdot [\text{CO}_2] \quad K_p = p_{\text{H}_2\text{O}} \cdot p_{\text{CO}_2}$$

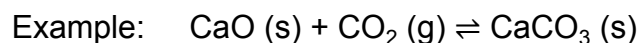
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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

4. Heterogeneous Equilibrium



$$K_c = \frac{1}{[\text{CO}_2]}$$

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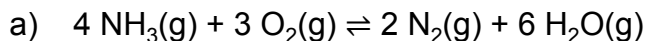
$$K_p = \frac{1}{P_{\text{CO}_2}}$$

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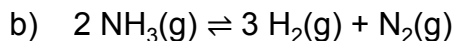
Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

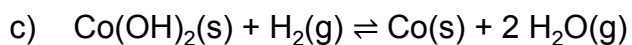
Write the proper expression for K_c for each of the following equilibria.



$$K_c = \frac{[\text{N}_2]^2 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^3}$$



$$K_c = \frac{[\text{H}_2]^3 [\text{N}_2]}{[\text{NH}_3]^2}$$



$$K_c = \frac{[\text{H}_2\text{O (g)}]^2}{[\text{H}_2 \text{ (g)}]}$$

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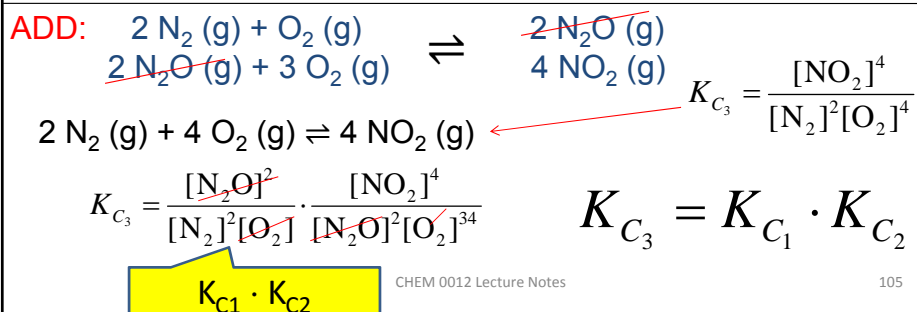
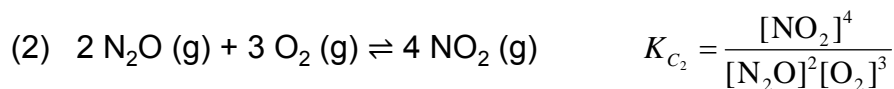
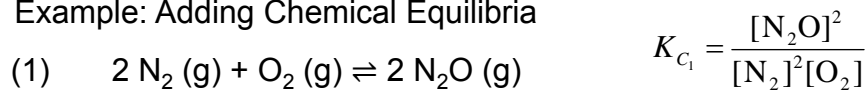
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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

5. Equilibrium laws for Combined Equilibrium

Example: Adding Chemical Equilibria



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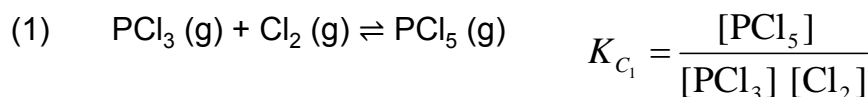
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Equilibrium Constant Expression and K_{eq}

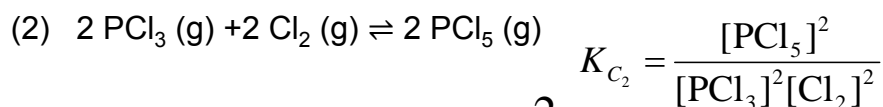
Hebden – Unit 2 (page 57-63)

5. Equilibrium laws for scaled equilibrium

Example: Multiply the coefficients by a factor



Multiply the coefficients by 2



$$K_{C_2} = K_{C_1}^2$$

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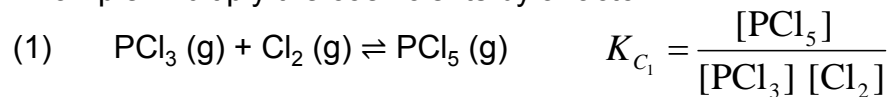
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Equilibrium Constant Expression and K_{eq}

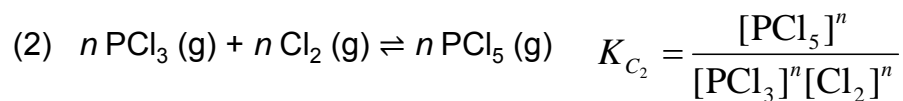
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5. Equilibrium laws for scaled equilibrium

Example: Multiply the coefficients by a factor



In general, multiply the coefficients by n



$$K_{C_2} = K_{C_1}^n$$

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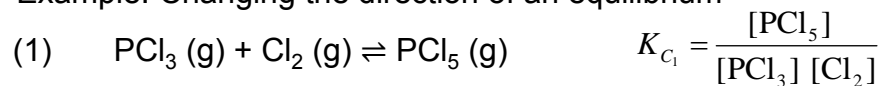
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Equilibrium Constant Expression and K_{eq}

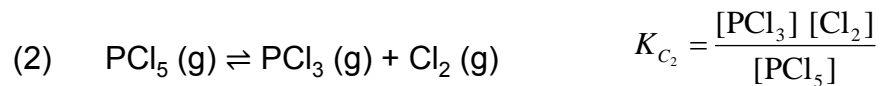
Hebden – Unit 2 (page 57-63)

5. Equilibrium laws for reversed equilibrium

Example: Changing the direction of an equilibrium



Reverse the direction



$$K_{C_2} = \frac{1}{K_{C_1}}$$

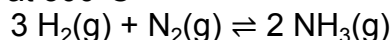
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Equilibrium Constant Expression and K_{eq}

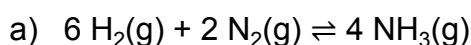
Hebden – Unit 2 (page 57-63)

Given at 300°C

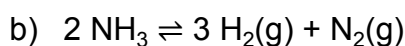


$$K_{C_1} = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]} = 9.5$$

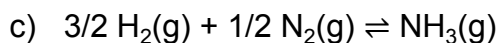
What is K_c for



$$K_C = (K_{C_1})^2 = (9.5)^2 = 90$$



$$K_C = \frac{1}{K_{C_1}} = \frac{1}{9.5} = 0.11$$



$$K_C = \sqrt{K_{C_1}} = \sqrt{9.5} = 3.1$$

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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

6. Interpreting K_{eq} values

- (i) Since K_{eq} represents the ratio between equilibrium concentrations of products to reactants

$$K_{eq} = \frac{[\text{Products}]}{[\text{Reactants}]}$$

- Large K_{eq} means the equilibrium favours the products (i.e. more products than reactants)
- Small K_{eq} means the equilibrium favours the reactants (i.e. more reactants than products)
- $K_{eq} \cong 1$ means reactants and products concentrations are nearly the same (midway) at equilibrium.

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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

6. Interpreting K_{eq} values

Reaction	K_p
$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(l)$	1.4×10^{83} @ 25°C
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	1.9×10^{-23} @ 25°C 1.0 @ 900°C
$2SO_2(s) + O_2(g) \rightleftharpoons 2SO_3(g)$	3.4 @ 700°C

$K \gg 1 \rightarrow [\text{products}] \gg [\text{reactants}] \rightarrow$ Reaction is product-favored

$K \ll 1 \rightarrow [\text{products}] \ll [\text{reactants}] \rightarrow$ Reaction is reactant-favored

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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

6. Interpreting K_{eq} values

$$K_{eq} = \frac{[\text{Products}]}{[\text{Reactants}]}$$

(ii) ONLY **TEMPERATURE** affects the value of K_{eq} .

- Increasing temperature for an **exothermic** reaction



shifts the equilibrium to the left, favouring the reactants. This results in increasing [Reactants], and K_{eq} becomes smaller.

- Increasing temperature for an **endothermic** reaction



shifts the equilibrium to the right, favouring the products. This results in increasing [Products], and K_{eq} becomes larger.

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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

6. Interpreting K_{eq} values

3. The following will have **NO effect** on the chemical equilibrium.

- (i) **Adding a catalyst** – No effect; A catalyst changes the rate of both the forward and reverse reactions to the same extent.
- (ii) **Adding a solid** – No effect; Concentration is omitted from the equilibrium expression.
- (iii) **Adding a pure liquid** - No effect; Concentration is omitted from the equilibrium expression.
- (iv) **Adding an inert gas under constant volume condition** – No effect; It affects the total pressure of the system. It has no effect on the partial pressures of the gases.

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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

7. Explain Le Chatelier's Principle mathematically with K_{eq} .

Recall Le Chatelier's Principle:

When a stress is applied to a closed system at equilibrium, the system will respond to **REDUCE** the stress and establish a new equilibrium.

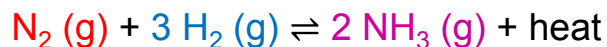
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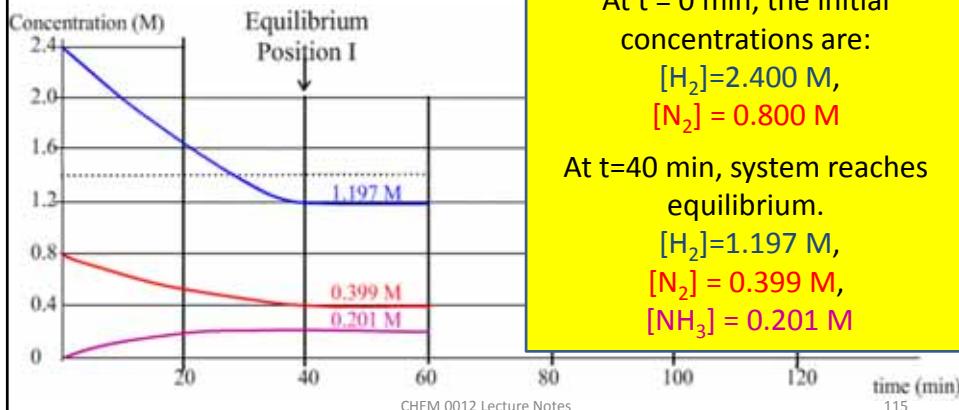
Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

Let's examine the "Concentration VS. Time" graph for



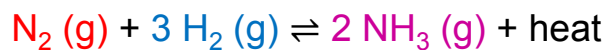
At constant temperature,



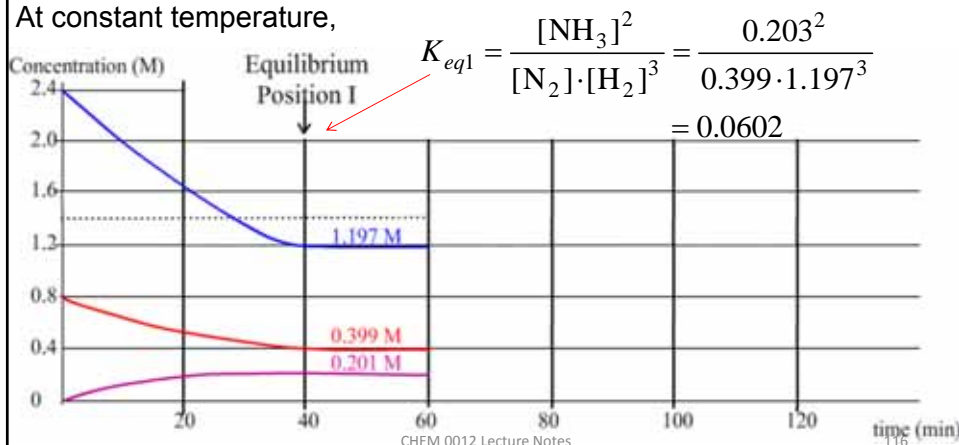
Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

Let's examine the "Concentration VS. Time" graph for



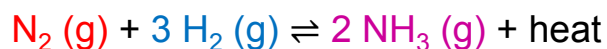
At constant temperature,



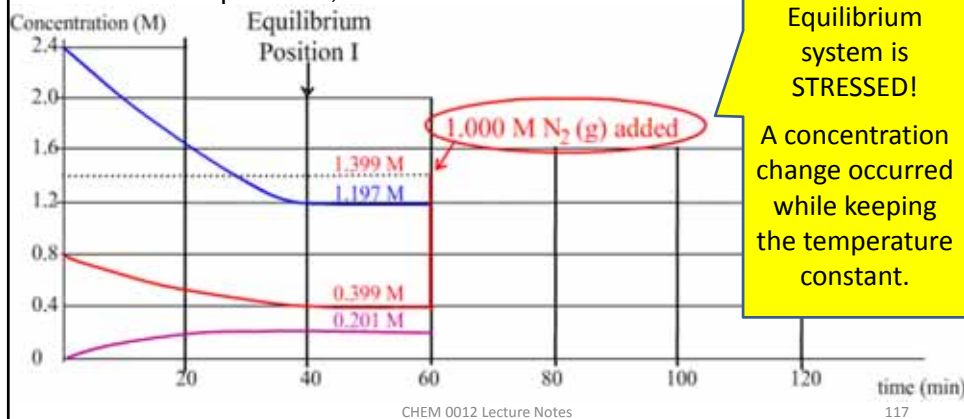
Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

Let's examine the "Concentration VS. Time" graph for



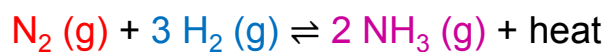
At constant temperature,



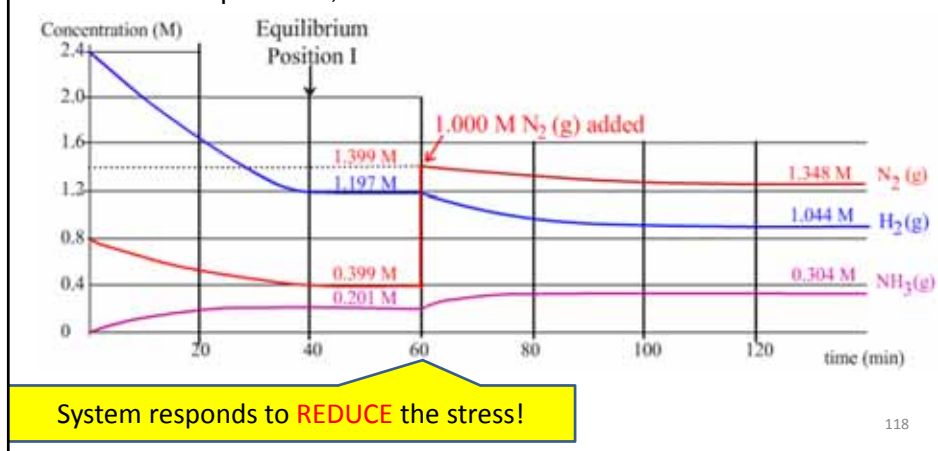
Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

Let's examine the "Concentration VS. Time" graph for



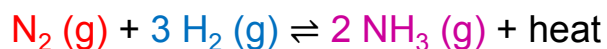
At constant temperature,



Equilibrium Constant Expression and K_{eq}

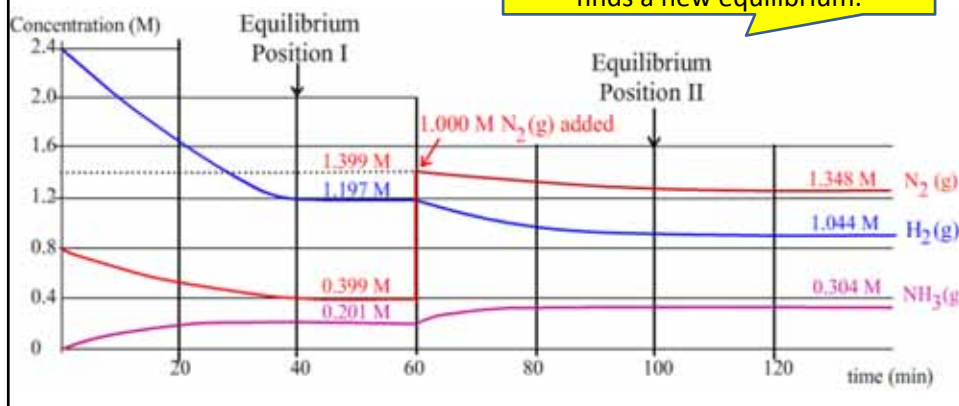
Hebden – Unit 2 (page 57-63)

Let's examine the "Concentration VS. Time" graph for



At constant temperature,

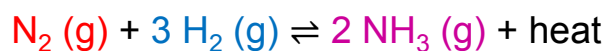
40 minutes later, the system finds a new equilibrium.



Le Chatelier's Principle – Effect of Concentration Change

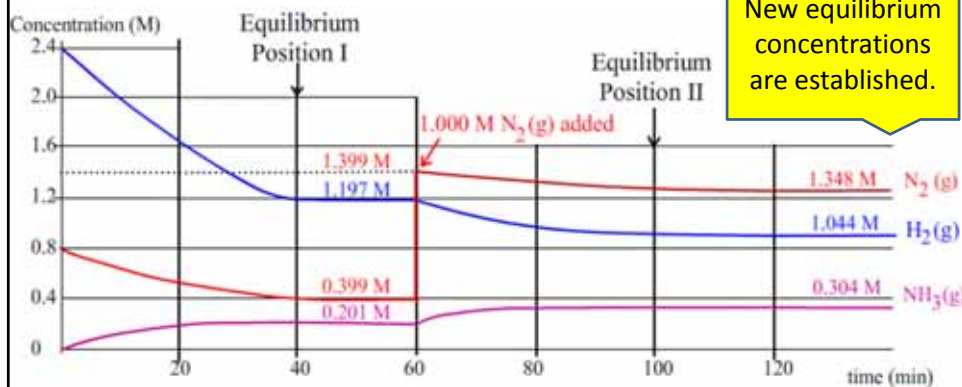
Hebden – Unit 2 (page 50-55)

Let's examine the "Concentration VS. Time" graph for



At constant temperature,

New equilibrium concentrations are established.



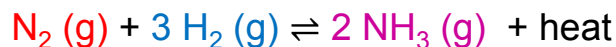
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Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

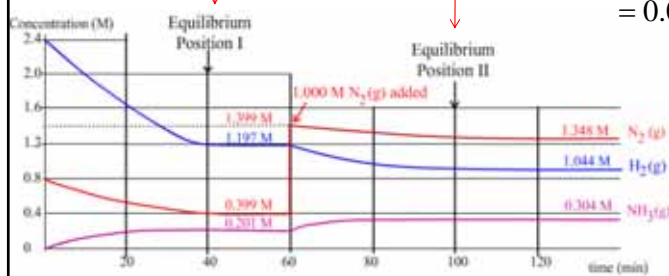
Let's examine the "Concentration VS. Time" graph for



At constant temperature,

$$K_{eq1} = \frac{0.203^2}{0.399 \cdot 1.197^3} = 0.0602$$

$$K_{eq2} = \frac{[\text{NH}_3]^2}{[\text{N}_2] \cdot [\text{H}_2]^3} = \frac{0.304^2}{1.348 \cdot 1.044^3} = 0.0602$$



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$$K_{eq1} = K_{eq2} = 0.0602$$

The system adjusts to reduce the stress such that the new equilibrium has the same K_{eq} same value.

Equilibrium Constant Expression and K_{eq}

Hebden – Unit 2 (page 57-63)

1. Equilibrium Constant Expression
2. Equilibrium Constant, K_{eq}
3. K_c and K_p
4. Heterogeneous equilibrium
5. Equilibrium laws for
 - Combined equilibrium
 - Scaled equilibrium
 - Reversed equilibrium
6. Interpreting K_{eq} values
7. Explain Le Chatelier's Principle mathematically with K_{eq} .

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Equilibrium

Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2
(page 37-69)

Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type I: Calculating the Equilibrium Constant

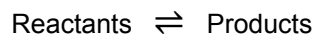
Type II: Calculating the Equilibrium Concentrations

Type III: Calculating the Equilibrium Concentrations
when a reagent is added

Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Consider the magnitude of K_{eq} and the position of equilibrium.



When K_{eq} is very large - Reaction proceeds towards completion. The position of equilibrium **lies far to the right**, toward the products.
($K_{eq} \gg 1$)

When $K_{eq} \cong 1$ - The concentrations of reactants and products are nearly the same at equilibrium. The position of equilibrium lies approximately **midway** between reactants and products.

When K_{eq} is very small - Extremely small amounts of products are formed. The position of equilibrium **lies far to the left**, toward the reactants.
($K_{eq} \ll 1$)

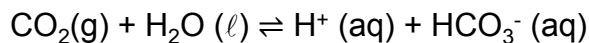
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type I: 1. Find the value of K_{eq} for the following equilibrium



when the equilibrium concentrations of:

$$[\text{CO}_2] = 0.16 \text{ M} \quad [\text{H}^+] = 0.38 \text{ M} \quad [\text{HCO}_3^-] = 3.0 \text{ M}$$

$$K_{eq} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = \frac{(0.38)(3.0)}{0.16} = 7.1$$

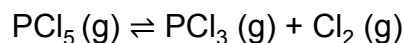
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type I: 2. Consider the equilibrium



Find K_{eq} if the system initially contained only

$[\text{PCl}_5] = 0.70 \text{ M}$ and the final $[\text{Cl}_2] = 0.15 \text{ M}$.

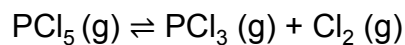
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type I: 2. Consider the equilibrium



Find K_{eq} if the system initially contained only

$[\text{PCl}_5] = 0.70 \text{ M}$ and the final $[\text{Cl}_2] = 0.15 \text{ M}$.

	$\text{PCl}_5(\text{g})$	\rightleftharpoons	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$	Given information
[I]	0.70		0		0	
[C]						
[E]					0.15	

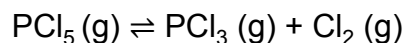
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type I: 2. Consider the equilibrium



Find K_{eq} if the system initially contained only

$[\text{PCl}_5] = 0.70 \text{ M}$ and the final $[\text{Cl}_2] = 0.15 \text{ M}$.

	$\text{PCl}_5(\text{g})$	\rightleftharpoons	$\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
[I]	0.70		0
[C]			+ 0.15
[E]			0.15

Solve for
Change in
 Cl_2

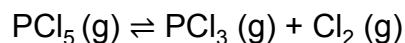
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type I: 2. Consider the equilibrium



Find K_{eq} if the system initially contained only

$[\text{PCl}_5] = 0.70 \text{ M}$ and the final $[\text{Cl}_2] = 0.15 \text{ M}$.

	$\text{PCl}_5(\text{g})$	\rightleftharpoons	$\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
[I]	0.70		0
[C]	- 0.15		+ 0.15
[E]			0.15

Solve for
Change in
 PCl_5 and
 PCl_3

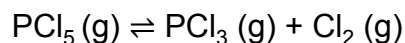
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type I: 2. Consider the equilibrium



Find K_{eq} if the system initially contained only

$[\text{PCl}_5] = 0.70 \text{ M}$ and the final $[\text{Cl}_2] = 0.15 \text{ M}$.

	$\text{PCl}_5(\text{g})$	\rightleftharpoons	$\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
[I]	0.70		0
[C]	- 0.15		+ 0.15
[E]	0.55		0.15

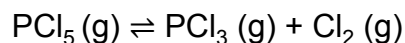
Solve for
Final
Concen-
trations

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type I: 2. Consider the equilibrium



Find K_{eq} if the system initially contained only

$[\text{PCl}_5] = 0.70 \text{ M}$ and the final $[\text{Cl}_2] = 0.15 \text{ M}$.

$$K_{eq} = \frac{[\text{Cl}_2] \cdot [\text{PCl}_3]}{[\text{PCl}_5]} = \frac{0.15 \cdot 0.15}{0.55} = 0.041$$

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type I: Equilibrium is established for the reaction



The quantities of the two gases present in a 3.00 liter vessel are 7.64 g N_2O_4 and 1.56 g NO_2 . What is the value of K for this reaction?

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type I: Equilibrium is established for the reaction



The quantities of the two gases present in a 3.00 liter vessel are 7.64 g N_2O_4 and 1.56 g NO_2 . What is the value of K for this reaction?

$$n_{\text{N}_2\text{O}_4} = (7.64 \text{ g } \text{N}_2\text{O}_4) \left(\frac{\text{mol } \text{N}_2\text{O}_4}{92.01 \text{ g } \text{N}_2\text{O}_4} \right) = 0.0830 \text{ mol } \text{N}_2\text{O}_4$$

$$[\text{N}_2\text{O}_4] = \frac{0.0830 \text{ mol } \text{N}_2\text{O}_4}{3.00 \text{ l}} = 0.0277 \text{ M } \text{N}_2\text{O}_4$$

$$n_{\text{NO}_2} = (1.56 \text{ g } \text{NO}_2) \left(\frac{\text{mol } \text{NO}_2}{46.01 \text{ g } \text{NO}_2} \right) = 0.0339 \text{ mol } \text{NO}_2$$

$$[\text{NO}_2] = \frac{0.0339 \text{ mol } \text{NO}_2}{3.00 \text{ l}} = 0.0113 \text{ M } \text{NO}_2$$

$$K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{[0.0113]^2}{[0.0277]} = 4.61 \times 10^{-3}$$

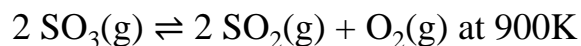
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type I: Equilibrium is established for the reaction



When a 0.0200 mol sample of $\text{SO}_3(\text{g})$ is introduced into a 1.52 liter vessel, 0.0142 mol of $\text{SO}_3(\text{g})$ is found to be present at equilibrium. What is the value of K for this reaction?

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type I: Equilibrium is established for the reaction

Equilibrium is established for the reaction

$2 \text{SO}_3(\text{g}) \rightleftharpoons 2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g})$ at 900K. When a 0.0200 mol sample of $\text{SO}_3(\text{g})$ is introduced into a 1.52 liter vessel, 0.0142 mol of $\text{SO}_3(\text{g})$ is found to be present at equilibrium. What is the value of K for this reaction?

Reaction	$2 \text{SO}_3(\text{g})$	\rightleftharpoons	$2 \text{SO}_2(\text{g})$	+	$\text{O}_2(\text{g})$
Initial amount	0.0200 mol		0.00 mol		0.00 mol
Change	-0.0058 mol		$+0.0058 \text{ mol}$		$+0.0029 \text{ mol}$
Equil. Amt.	0.0142 mol		0.0058 mol		0.0029 mol
Equil. Conc.	$9.34 \times 10^{-3} \text{ M}$		$3.8 \times 10^{-3} \text{ M}$		$1.9 \times 10^{-3} \text{ M}$

$$K = \frac{[\text{SO}_2]^2 [\text{O}_2]}{[\text{SO}_3]^2} = \frac{[3.8 \times 10^{-3}]^2 [1.9 \times 10^{-3}]}{[9.34 \times 10^{-3}]^2} = 3.1 \times 10^{-4}$$

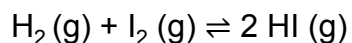
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type II: 3. Consider the equilibrium



The $K_{eq} = 50.$ at a certain temperature. Find the equilibrium concentration of HI, if at equilibrium $[\text{H}_2] = 0.50 \text{ M}$, $[\text{I}_2] = 0.50 \text{ M}$.

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2 \text{HI}(\text{g})$
[I]	-		-		-
[C]	-		-		-
[E]	0.50		0.50		x

Equilibrium
Concen-
trations

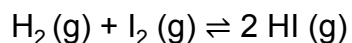
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type II: 3. Consider the equilibrium



The $K_{eq} = 50.$ at a certain temperature. Find the equilibrium concentration of HI, if at equilibrium $[\text{H}_2] = 0.50 \text{ M}$, $[\text{I}_2] = 0.50 \text{ M}$.

$$K_{eq} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{x^2}{(0.50)(0.50)} = 50$$

$$x = \sqrt{(0.50)^2 (50)} = \pm 3.5$$

Since $x = [\text{HI}]$, $x > 0 \therefore x = [\text{HI}] = 3.5 \text{ M}$

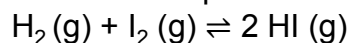
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type II: 4. Consider the equilibrium



The $K_{eq} = 50.$ at a certain temperature. What are the equilibrium concentrations of each substance if a 2.0 L flask that initially contains only 1.0 mole H_2 and 1.0 mole I_2 . Assume the same temperature is maintained.

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2 \text{HI}(\text{g})$
[I]	1 mole/2.0 L = 0.50		1 mole/2.0 L = 0.50		0
[C]					
[E]					

Given
Information

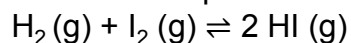
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type II: 4. Consider the equilibrium



The $K_{eq} = 50.$ at a certain temperature. What are the equilibrium concentrations of each substance if a 2.0 L flask that initially contains only 1.0 mole H_2 and 1.0 mole I_2 . Assume the same temperature is maintained.

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2 \text{HI}(\text{g})$
[I]	1 mole/2.0 L = 0.50		1 mole/2.0 L = 0.50		0
[C]	- x		- x		+2 x
[E]					

Stoichio-
metric
ratio

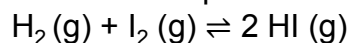
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type II: 4. Consider the equilibrium



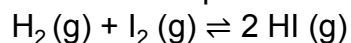
The $K_{eq} = 50$. at a certain temperature. What are the equilibrium concentrations of each substance if a 2.0 L flask that initially contains only 1.0 mole H_2 and 1.0 mole I_2 . Assume the same temperature is maintained.

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2 \text{HI}(\text{g})$	
[I]	1 mole/2.0 L = 0.50		1 mole/2.0 L = 0.50		0	Equilibrium Concentrations
[C]	- x		- x		+2 x	
[E]	0.50 - x		0.50 - x		2 x	

Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type II: 4. Consider the equilibrium



The $K_{eq} = 50$. at a certain temperature. What are the equilibrium concentrations of each substance if a 2.0 L flask that initially contains only 1.0 mole H_2 and 1.0 mole I_2 . Assume the same temperature is maintained.

$$K_{eq} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(0.50-x)^2} = 50$$

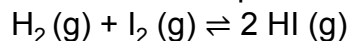
$$\frac{(2x)}{(0.50-x)} = \pm \sqrt{50} \quad \text{or} \quad x = \frac{\pm(0.50)\sqrt{50}}{2 \pm \sqrt{50}} = 0.39 \text{ M}, -0.70 \text{ M}$$

$$\text{Since } 2x = [\text{HI}], x > 0, \quad \therefore x = 0.39 \text{ M}$$

Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type II: 4. Consider the equilibrium



The $K_{eq} = 50.$ at a certain temperature. What are the equilibrium concentrations of each substance if a 2.0 L flask that initially contains only 1.0 mole H_2 and 1.0 mole I_2 . Assume the same temperature is maintained.

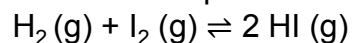
	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2 \text{HI}(\text{g})$
[I]	1 mole/2.0 L = 0.50		1 mole/2.0 L = 0.50		0
[C]	- x		- x		+2 x
[E]	0.50 - 0.39		0.50 - 0.39		2(0.39)

Calculate equilibrium concentrations

Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type II: 4. Consider the equilibrium



The $K_{eq} = 50.$ at a certain temperature. What are the equilibrium concentrations of each substance if a 2.0 L flask that initially contains only 1.0 mole H_2 and 1.0 mole I_2 . Assume the same temperature is maintained.

$$[\text{H}_2] = 0.50 - 0.39 = 0.11 \text{ M}$$

$$[\text{I}_2] = 0.50 - 0.39 = 0.11 \text{ M}$$

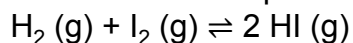
$$[\text{HI}] = 2(0.39) = 0.78 \text{ M}$$

Substitute these equilibrium concentration into the equilibrium constant expression to confirm that $K_{eq} = 50.$

Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type III: 5. Consider the equilibrium.



What are the final equilibrium concentrations of each substance if a 0.50 L flask initially contains 2.0 moles H_2 , 1.0 mole I_2 and 10. mole HI, then 1.0 mole I_2 is added.

	$\text{H}_2 (\text{g})$	+	$\text{I}_2 (\text{g})$	\rightleftharpoons	$2 \text{HI} (\text{g})$
[I]	2.0 mole/0.50 L = 4.0 M		1.0 mole/0.50 L = 2.0 M		10 mole/0.50 L = 20. M
[A]			1.0 mole/0.50 L = 2.0 M		
[C]					
[E]					

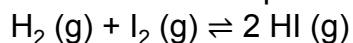
Given
information

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type III: 5. Consider the equilibrium.



What are the final equilibrium concentrations of each substance if a 0.50 L flask initially contains 2.0 moles H_2 , 1.0 mole I_2 and 10. mole HI, then 1.0 mole I_2 is added.

	$\text{H}_2 (\text{g})$	+	$\text{I}_2 (\text{g})$	\rightleftharpoons	$2 \text{HI} (\text{g})$
[I]	2.0 mole/0.50 L = 4.0 M		1.0 mole/0.50 L = 2.0 M		10 mole/0.50 L = 20. M
[A]			1.0 mole/0.50 L = 2.0 M		
[C]	- x		- x		+2x
[E]	4.0 - x		4.0 - x		20. +2x

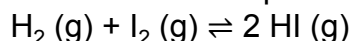
Equilibrium
concentrations

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type III: 5. Consider the equilibrium.



What are the final equilibrium concentrations of each substance if a 0.50 L flask initially contains 2.0 moles H_2 , 1.0 mole I_2 and 10. mole HI, then 1.0 mole I_2 is added.

$$K_{eq} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(20. + 2x)^2}{(4 - x)^2} = 50$$

$$\frac{(20 + 2x)}{(4 - x)} = \pm \sqrt{50} \quad \text{or} \quad x = \frac{\pm 4\sqrt{50} - 20}{2 \pm \sqrt{50}} = 0.91 \text{ M}, 9.5 \text{ M}$$

Since $4 - x = [\text{H}_2]$, $x < 4$, $\therefore x = 0.91 \text{ M}$

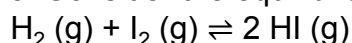
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type III: 5. Consider the equilibrium.



What are the final equilibrium concentrations of each substance if a 0.50 L flask initially contains 2.0 moles H_2 , 1.0 mole I_2 and 10. mole HI, then 1.0 mole I_2 is added.

$$[\text{H}_2] = 4.0 - 0.91 = 3.09 \text{ M}$$

$$[\text{I}_2] = 4.0 - 0.91 = 3.09 \text{ M}$$

$$[\text{HI}] = 20. + 2(0.91) = 21.8 \text{ M}$$

The addition of I_2 resulted in a shift to the right.

Substitute these equilibrium concentration into the equilibrium constant expression to confirm that $K_{eq} = 50$.

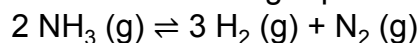
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type II: 6. Consider the following equilibrium at 25°C.



Initially a 5.0 L flask contains only 1.0 mole NH_3 and 0.40 mole N_2 . After equilibrium is established, 0.78 mole NH_3 remain. Find the new equilibrium concentrations of H_2 and the value of K_{eq} .

	$2 \text{NH}_3 (\text{g}) \rightleftharpoons 3 \text{H}_2 (\text{g}) + \text{N}_2 (\text{g})$		
[I]	1.0 mole/5.0 L = 0.20 M	0 M	0.40 mole/5.0 L = 0.08 M
[C]			
[E]	0.78/5 = 0.156 M		

Given
informa-
tion

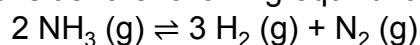
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type II: 6. Consider the following equilibrium at 25°C.



Initially a 5.0 L flask contains only 1.0 mole NH_3 and 0.40 mole N_2 . After equilibrium is established, 0.78 mole NH_3 remain. Find the new equilibrium concentrations of H_2 and the value of K_{eq} .

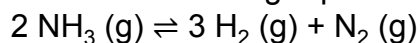
	$2 \text{NH}_3 (\text{g}) \rightleftharpoons 3 \text{H}_2 (\text{g}) + \text{N}_2 (\text{g})$		
[I]	1.0 mole/5.0 L = 0.20 M	0 M	0.40 mole/5.0 L = 0.08 M
[C]	-0.044 M	$3/2(0.044) =$ 0.066 M	$0.044/2 =$ 0.022 M
[E]	0.78/5 = 0.156 M	0.066 M	0.102 M

Equilibrium
Conditions

Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type II: 6. Consider the following equilibrium at 25°C.



Initially a 5.0 L flask contains only 1.0 mole NH_3 and 0.40 mole N_2 . After equilibrium is established, 0.78 mole NH_3 remain. Find the new equilibrium concentrations of H_2 and the value of K_{eq} .

$$K_{eq} = \frac{[\text{H}_2]^3 [\text{N}_2]}{[\text{NH}_3]^2} = \frac{(0.102)(0.066)^3}{(0.156)^2} = 0.00121$$

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

We have covered this three types of K_{eq} calculations in this presentation.

Type I: Calculating the Equilibrium Constant

Type II: Calculating the Equilibrium Concentrations

Type III: Calculating the Equilibrium Concentrations
when a reagent is added

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type I: Calculating the Equilibrium Constant

Type II: Calculating the Equilibrium Concentrations

Type III: Calculating the Equilibrium Concentrations
when a reagent is added

Type IV: Determining the shift and/or calculating
more than one variable (K_{eq} and Concentration)

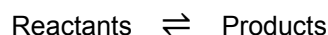
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Consider the magnitude of K_{eq} and the position of equilibrium.



When K_{eq} is very large - Reaction proceeds towards completion. The position of
($K_{eq} \gg 1$) equilibrium **lies far to the right**, toward the products.

When $K_{eq} \approx 1$ - The concentrations of reactants and products are nearly the
same at equilibrium. The position of equilibrium lies
approximately **midway** between reactants and products.

When K_{eq} is very small - Extremely small amounts of products are formed. The
($K_{eq} \ll 1$) position of equilibrium **lies far to the left**, toward the
reactants.

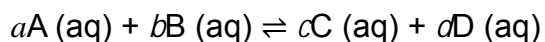
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

For non-equilibrium conditions, K is replaced by the reaction quotient, Q .



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

What is Q and what does Q have to do with K_{eq} ?

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Depending on the relationship between Q and K , one can predict the direction the reaction will shift until equilibrium is achieved. There are three conditions, which should be considered.

$Q = K_{eq}$, then the reaction is at equilibrium.

$Q > K_{eq}$, then the reaction is not at equilibrium and some products will be converted to reactants.

$Q < K_{eq}$, then the reaction is not at equilibrium and some reactants will be converted to products.

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

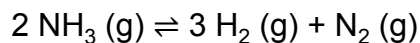
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type IV: 7. Consider the following equilibrium at 25°C.



2.0 L flask initially contains 2.5 M $\text{NH}_3 (\text{g})$, 0.40 M $\text{H}_2 (\text{g})$, 0.50 M $\text{N}_2 (\text{g})$. Show which way will the system shift to reach equilibrium. From example 6, $K_{eq} = 0.00121$

	$2 \text{NH}_3 (\text{g})$	\rightleftharpoons	$3 \text{H}_2 (\text{g})$	+	$\text{N}_2 (\text{g})$
[I]	2.5 M		0.40 M		0.50 M

$$Q = \frac{[\text{H}_2]^3 [\text{N}_2]}{[\text{NH}_3]^2} = \frac{(0.40)^3 (0.50)}{(2.5)^2} = 0.00512$$

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Compare Q to K_{eq} .

$$Q = 0.00512 \quad K_{eq} = 0.00121^*$$

$Q = K_{eq}$, then the reaction is at equilibrium.

$Q > K_{eq}$, then the reaction is not at equilibrium and some products will be converted to reactants.

$Q < K_{eq}$, then the reaction is not at equilibrium and some reactants will be converted to products.

Equilibrium will adjust to convert products to reactant, shift to the left.

* Calculated in example 6.

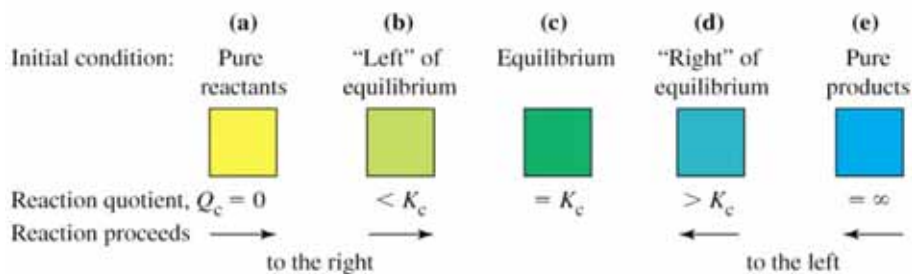
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Compare Q to K_{eq} ,



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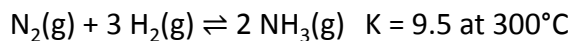
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Predicting the Direction of Net Change Example

Consider the equilibrium among $N_2(g)$, $H_2(g)$ and $NH_3(g)$ in 1 liter flask.



n_{N_2}	n_{H_2}	n_{NH_3}	Q	Shift	mass NH_3 \uparrow or \downarrow
1	1	1			
1.7	0.3	1			
0.3	1.7	1			

Place the last mixture in a 10 liter flask (conc. \downarrow by a factor of 10)

0.3	1.7	1
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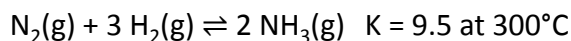
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Predicting the Direction of Net Change Example

Consider the equilibrium among $N_2(g)$, $H_2(g)$ and $NH_3(g)$ in 1 liter flask.



n_{N_2}	n_{H_2}	n_{NH_3}	Q	Shift	mass NH_3 ↑ or ↓
1	1	1	1	→	↑
1.7	0.3	1	20	←	↓
0.3	1.7	1	0.7	→	↑
Place the last mixture in a 10 liter flask (conc. ↓ by a factor of 10)					
0.3	1.7	1	70	←	↓

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

We can make assumptions to simplify the math.

Equilibrium calculations can usually be simplified when K_{eq} is very small (ie – position of the equilibrium lies far to the left), toward the reactants. Usually this permits us to simplify the calculations considerably.

example: $0.100 - x \cong 0.100$

where 0.100 is the initial reactant concentration and the amount of dissociation, x , is small. This is valid if the initial reactant concentration of 0.100 is at least $1000 \times K_{eq}$. But always check to see if the assumption is valid.

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

$$\frac{[initial]}{K_{eq}} > 1000$$

Sometimes assumptions can be made to simplify the math of the problems. Any time that an assumption is made, the validity of the assumption must be checked. If it is not valid, the quadratic equation should be used.

The quadratic equation will be given in an exam.

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

The quadratic equation is used to determine the value of x when x is in a mathematical equation in this form:

$$ax^2 + bx + c = 0$$

where a, b and c are numbers ($a \neq 0$). The quadratic equation is then set up to solve for x:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

The quadratic equation will give two possible values of x ,

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

one from the + sign up and one from the – sign in the numerator. Only one of these values will be correct.

The incorrect value is usually obvious because it is usually results in a negative concentration.

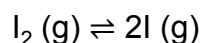
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Type IV: 8. The equilibrium constant for the dissociation of iodine, $I_2(g)$, is 3.76×10^{-3} at 1000 K.



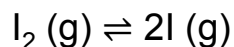
Suppose 1.00 mole of iodine is placed in a 2.00 L flask at 1000 K. What are the concentrations of iodine and the iodine atom when the system comes to equilibrium?

	$I_2(g)$	\rightleftharpoons	$2 I(g)$	Stoichiometric ratio
[I]	1 mole/2.0 L = 0.50 M		0	
[C]	-x		+2x	
[E]	0.50 - x		2x	

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)



$$K_{eq} = \frac{[\text{I}]^2}{[\text{I}_2]} = \frac{(2x)^2}{(0.500 - x)} = 3.76 \times 10^{-3}$$

Test to see if we can simplify.

We can simplify if $\frac{[\text{initial}]}{K_{eq}} > 1000$

$$\frac{0.500}{3.76 \times 10^{-3}} = 132.98 \quad (< 1000)$$

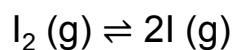
We cannot simplify! We need to use the quadratic equation to solve for x .

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)



$$K_{eq} = \frac{[\text{I}]^2}{[\text{I}_2]} = \frac{(2x)^2}{(0.500 - x)} = 3.76 \times 10^{-3}$$

Rearrange,

$$3.76 \times 10^{-3} (0.500 - x) = 4x^2$$

$$0.00188 - (3.76 \times 10^{-3})x = 4x^2$$

$$4x^2 + (3.76 \times 10^{-3})x - 0.00188 = 0$$

$$a = 4, b = 3.76 \times 10^{-3}, c = -0.00188$$

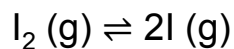
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)



$$K_{eq} = \frac{[I]^2}{[I_2]} = \frac{(2x)^2}{(0.500 - x)} = 3.76 \times 10^{-3}$$

Use the quadratic formula.

$$a = 4, b = 3.76 \times 10^{-3}, c = -0.00188$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = 0.0212, -0.02215$$

Compare:
If we had made the assumption that $0.500 - x \approx 0.500$ then $x = 0.0218$

$$\begin{aligned} [I_2] &= 0.500 - 0.0212 \\ &= 0.479 \text{ M} \\ [I] &= 0.0424 \text{ M} \end{aligned}$$

Check:

$$K_{eq} = \frac{(0.0424)^2}{(0.479)} = 3.76 \times 10^{-3}$$

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

We have covered the following type of K_{eq} calculation in this presentation.

Type IV: Determining the shift and/or calculating more than one variable (K_{eq} and Concentration)

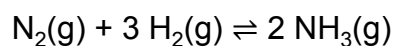
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Equilibrium Constant, K_{eq} , Calculations

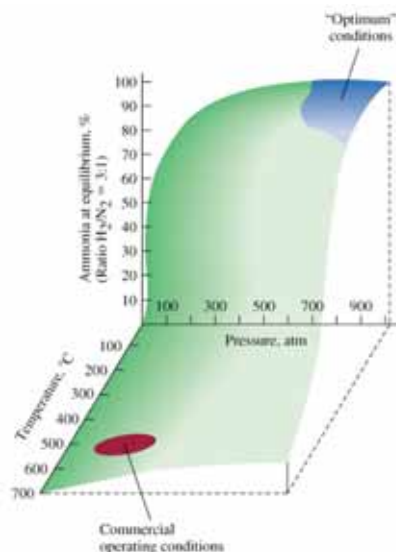
Hebden – Unit 2 (page 57-63)

Synthesis of NH_3



$$\Delta H = -92 \text{ kJ/mol}$$

The optimum conditions are only for the equilibrium position and do not take into account the *rate* at which equilibrium is attained.



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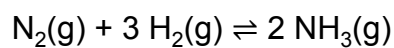
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Equilibrium Constant, K_{eq} , Calculations

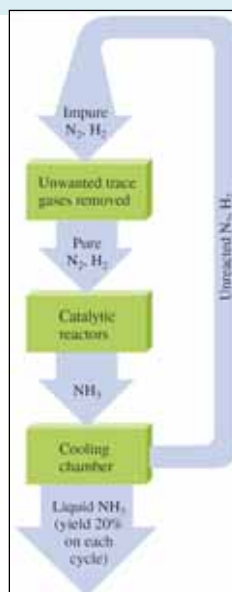
Hebden – Unit 2 (page 57-63)

Schematic Diagram of the Haber Process

Synthesis of NH_3



$$\Delta H = -92 \text{ kJ/mol}$$



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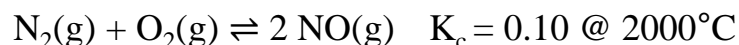
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:

Consider the following reaction



A reaction mixture at 2000°C initially contains

$[\text{N}_2] = 0.200 \text{ M}$ and $[\text{O}_2] = 0.200 \text{ M}$. Find the equilibrium concentrations of reactants and products at this temperature.

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:

	$\text{N}_2(\text{g})$	+	$\text{O}_2(\text{g})$	\rightleftharpoons	$2 \text{NO}(\text{g})$
I	0.200		0.200		0
C	$-x$		$-x$		$2x$
E	$0.200-x$		$0.200-x$		$2x$

$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(2x)^2}{(0.200-x)^2} = 0.10$$

$$\frac{(2x)}{(0.200-x)} = \pm \sqrt{0.10}$$

but this is the ratio of two concentrations so it is the positive root

$$x = \frac{+(0.200)\sqrt{0.10}}{2 + \sqrt{0.10}} = 0.027 \text{ M}$$

$$[\text{N}_2] = [\text{O}_2] = 0.200 \text{ M} - 0.027 \text{ M} = 0.173 \text{ M}, [\text{NO}] = 2(0.027 \text{ M}) = 0.054 \text{ M}$$

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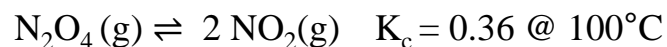
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:

Consider the following reaction



A reaction mixture at 100°C initially contains

$[\text{NO}_2] = 0.100 \text{ M}$. Find the equilibrium concentrations of reactants and products at this temperature.

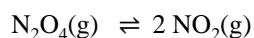
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:



I	0	0.100
C	x	$-2x$
E	x	$0.100-2x$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.100-2x)^2}{x} = \frac{0.0100-0.400x+4x^2}{x} = 0.36$$

$$4x^2 - 0.760x + 0.0100 = 0$$

$$x = \frac{-(-0.760) \pm \sqrt{(-0.760)^2 - 4(4)(0.0100)}}{2(4)} = 0.176 \text{ M}, 0.0142 \text{ M}$$

$x = 0.176 \text{ M}$ gives $[\text{NO}_2] < 0$ so $x = 0.0142 \text{ M}$

$[\text{N}_2\text{O}_4] = 0.0142 \text{ M}$, $[\text{NO}_2] = 0.100 \text{ M} - 2(0.0142 \text{ M}) = 0.072 \text{ M}$

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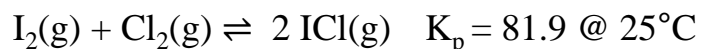
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:

Consider the following reaction



A reaction mixture at 25°C initially contains

$P_{\text{I}_2} = 0.100 \text{ atm}$, $P_{\text{Cl}_2} = 0.100 \text{ atm}$ and $P_{\text{ICl}} = 0.100 \text{ atm}$. Find the equilibrium pressures of reactants and products at this temperature.

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:

	$\text{I}_2(\text{g})$	+	$\text{Cl}_2(\text{g})$	\rightleftharpoons	$2\text{ICl}(\text{g})$
I	0.100		0.100		0.100
C	-x		-x		2x
E	0.100-x		0.100-x		0.100+2x

$$K_p = \frac{[\text{ICl}]^2}{[\text{I}_2][\text{Cl}_2]} = \frac{(0.100 + 2x)^2}{(0.100 - x)^2} = 81.9$$

$$\frac{(0.100 + 2x)}{(0.100 - x)} = \pm \sqrt{81.9}$$

but this is the ratio of two concentrations so it is the positive root

$$x = \frac{+(0.100)\sqrt{81.9} - 0.100}{2 + \sqrt{81.9}} = 0.0729 \text{ atm}$$

$$[\text{I}_2] = [\text{Cl}_2] = 0.100 - 0.0729 = 0.027 \text{ atm},$$

$$[\text{ICl}] = 0.100 + 2(0.0729) = 0.246 \text{ atm}$$

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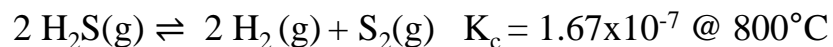
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:

Consider the following reaction



A 0.500 L reaction vessel at 800°C initially contains 1.25×10^{-2} mol H_2S . Find the equilibrium concentrations of reactants and products at this temperature.

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:

	$\text{H}_2\text{S}(\text{g})$	\rightleftharpoons	$2\text{H}_2(\text{g})$	+	$\text{S}_2(\text{g})$
I	0.0250		0		0
C	-2x		2x		x
E	0.0250-2x		2x		x

$$K_c = 1.67 \times 10^{-7} = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2} = \frac{(2x)^2 x}{(0.0250 - x)^2} \approx \frac{4x^3}{(0.0250)^2} \text{ assume } |x| \ll 0.025$$

$$x = \sqrt[3]{\frac{(0.0250)^2 (1.67 \times 10^{-7})}{4}} = 2.97 \times 10^{-4}$$

assumption is OK

$$[\text{H}_2\text{S}] = 0.0250 - 2(2.97 \times 10^{-4}) = 0.0244 \text{ M}$$

$$[\text{H}_2] = 2(2.97 \times 10^{-4}) = 5.94 \times 10^{-4} \text{ M}, \quad [\text{S}_2] = 2.97 \times 10^{-4} \text{ M}$$

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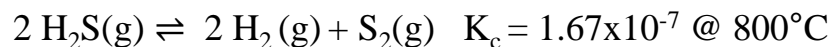
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:

Consider the following reaction



A 0.500 L reaction vessel at 800°C initially contains 1.25×10^{-4} mol H_2S . Find the equilibrium concentrations of reactants and products at this temperature.

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:

	$\text{H}_2\text{S}(\text{g})$	\rightleftharpoons	$2\text{H}_2(\text{g})$	+	$\text{S}_2(\text{g})$
I	2.50×10^{-4}		0		0
C	$-2x$		$2x$		x
E	$2.50 \times 10^{-4} - 2x$		$2x$		x

$$K_c = 1.67 \times 10^{-7} = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2} = \frac{(2x)^2 x}{(2.50 \times 10^{-4} - x)^2} = \frac{4x^3}{(2.50 \times 10^{-4} - x)^2}$$

$$x = \sqrt[3]{\frac{(2.50 \times 10^{-4} - x)^2 (1.67 \times 10^{-7})}{4}}$$

solve by successive approximations

x_0	x_1
0	1.377×10^{-5}
1.377×10^{-5}	1.274×10^{-5}
1.274×10^{-5}	1.282×10^{-5}
1.282×10^{-5}	1.281×10^{-5}
1.281×10^{-5}	1.281×10^{-5}

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:

	$H_2S(g)$	\rightleftharpoons	$2H_2(g)$	+	$S_2(g)$
I	2.50×10^{-4}		0		0
C	$-2x$		$2x$		x
E	$2.50 \times 10^{-4} - 2x$		$2x$		x

$$K_c = 1.67 \times 10^{-7} = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{(2x)^2 x}{(2.50 \times 10^{-4} - x)^2} = \frac{4x^3}{(2.50 \times 10^{-4} - x)^2}$$

$$x = \sqrt[3]{\frac{(2.50 \times 10^{-4} - x)^2 (1.67 \times 10^{-7})}{4}}$$

solved by successive approximations

$$x = 1.28 \times 10^{-5} \text{ M}$$

$$[H_2S] = 2.50 \times 10^{-4} - 2(1.28 \times 10^{-5}) = 2.24 \times 10^{-4} \text{ M}$$

$$[H_2] = 2(1.28 \times 10^{-5}) = 2.56 \times 10^{-5} \text{ M}, [S_2] = 1.28 \times 10^{-5} \text{ M}$$

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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:

Consider the following reaction



A 0.0240 mol sample of $N_2O_4(g)$ is allowed to dissociate and come to equilibrium with $NO_2(g)$ in an 0.372 liter flask at $25^\circ C$. What is the percent dissociation of the N_2O_4 ?

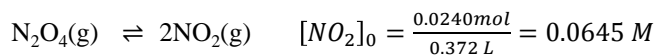
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:



I	0.0645	0
C	-x	2x
E	0.0645-x	2x

$$K_c = 4.61 \times 10^{-3} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(2x)^2}{0.0645 - x} = \frac{4x^2}{0.0645 - x}$$

$$4x^2 + (4.61 \times 10^{-3})x - 2.97 \times 10^{-4} = 0$$

$$x = \frac{-4.61 \times 10^{-3} \pm \sqrt{(4.61 \times 10^{-3})^2 - 4(4)(-2.97 \times 10^{-4})}}{2(4)}$$

$$x = 8.07 \times 10^{-3}, -9.22 \times 10^{-3} \text{ since } [\text{NO}_2] = 2x, x \geq 0, \therefore x = 8.07 \times 10^{-3} \text{ M}$$

$$\% \text{ dissociation} = \frac{x}{[\text{N}_2\text{O}_4]_0} = \frac{8.07 \times 10^{-3} \text{ M}}{0.0645 \text{ M}} = 12.5\%$$

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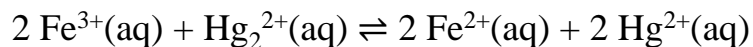
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:

Consider the following reaction



$$K = 9.14 \times 10^{-6}$$

A 25° C solution is prepared having initial concentrations:

$$[\text{Fe}^{3+}] = [\text{Hg}_2^{2+}] = 0.5000 \text{ M}; [\text{Fe}^{2+}] = [\text{Hg}^{2+}] = 0.03000 \text{ M}$$

What will be the ionic concentrations when equilibrium is reached?

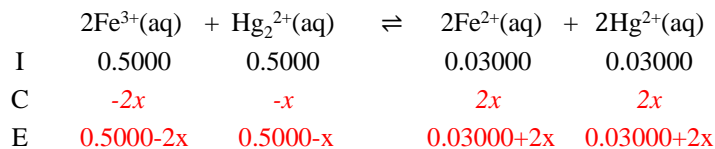
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:



$$K = 9.14 \times 10^{-6} = \frac{[Fe^{2+}]^2 [Hg_2^{2+}]^2}{[Fe^{3+}]^2 [Hg_2^{2+}]^2} = \frac{(0.03000 + 2x)^2 (0.03000 + 2x)^2}{(0.5000 - 2x)^2 (0.5000 - x)^2}$$

$$K = 9.14 \times 10^{-6} \approx \frac{(0.03000 + 2x)^4}{(0.5000)^3} \text{ assume } |2x| \ll 0.5000$$

$$(0.03000 + 2x) = \sqrt[4]{(0.5000)^3 (9.14 \times 10^{-6})} = 0.0327$$

note $0.03000 + 2x = [Fe^{2+}]$ so it must be a non - negative real number

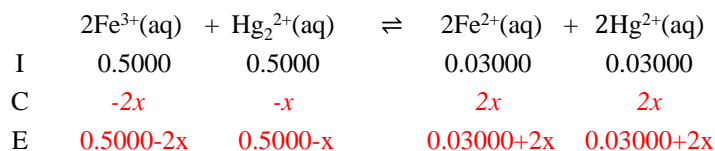
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:



$$(0.03000 + 2x) = 0.0327$$

$$\rightarrow 2x = 0.0027, x = 0.0014$$

$$[Fe^{2+}] = [Hg_2^{2+}] = 0.0327 M$$

$$[Fe^{2+}] = 0.5000 - 0.0027 = 0.4973 M$$

$$[Hg_2^{2+}] = 0.5000 - 0.0014 = 0.4986 M$$

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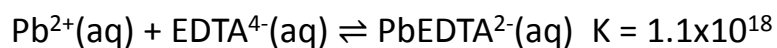
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:

Solutions of $EDTA^{4-}$ are used to treat heavy metal poisoning by removing the heavy metal in the form of a soluble complex ion. The reaction of $EDTA^{4-}$ with Pb^{2+} is



Consider a 1.00 L solution that is 0.050 M $EDTA^{4-}$ that has 0.010 mol of Pb^{2+} added to it. What is the concentration of Pb^{2+} ?

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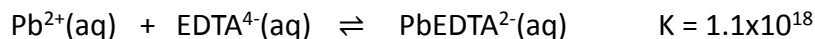
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Equilibrium Constant, K_{eq} , Calculations

Hebden – Unit 2 (page 57-63)

Problems:

Let reaction go to completion and then start approach to equilibrium



I	0.010	0.050	0
R	-0.010	-0.010	0.010
C	x	x	-x
E	x	0.040+x	0.010-x

$$K = 1.1 \times 10^{18} = \frac{[PbEDTA^{2-}]}{[Pb^{2+}][EDTA^{4-}]} = \frac{0.010 - x}{(x)(0.040 + x)} \approx \frac{0.010}{0.040x} \text{ assume } |x| \ll 0.010$$

$$x = \frac{0.010}{(0.040)(1.1 \times 10^{18})} = 2.3 \times 10^{-19} M \text{ assumption is OK}$$

$$[Pb^{2+}] = 2.3 \times 10^{-19} M$$

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