

Dynamic Equilibrium

A reversible reaction is at equilibrium if the rates of the forward and reverse reactions are equal.

The system will seem macroscopically static (constant properties), but be active microscopically (dynamic).

A Chemical equilibrium must:

1. Be a closed system (for matter).
2. Have observable properties constant.
3. Have a reversible reaction with forward and reverse rates equal.

Note: Systems are often kept at constant temperature (isothermal) by adding or removing heat.

1. Closed system:

Products and reactants must be contained so forward and reverse reactions can occur.

A gaseous reaction in a sealed container

A solid, liquid or aqueous reaction in a beaker

Phase equilibrium in a sealed container

2. Observable properties are constant (macroscopic properties)

An undisturbed system at equilibrium will look as if nothing is occurring or changing.

How can you determine if a system is in dynamic equilibrium, or not reacting at all?

3. Forward and reverse reaction rates are equal.

Must have a reversible reaction.

What does this mean about the E_a of a reaction?

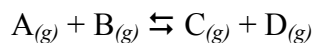
What role can a catalyst play?

Forward and reverse rates must be equal. This is symbolized with “ \rightleftharpoons ”

What if forward and reverse rates are not equal?

IB Chemistry — Equilibrium

Consider the reversible reaction:



What will happen if we put only some A and B in an empty sealed container?

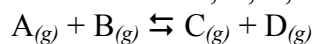
What will happen to:

Concentration of all species?

Forwards and reverse rates?

What will happen if we put only some C and D in a sealed container?

Consider the reversible reaction that is already at an equilibrium with some of A, B, C, and D in the container:



What will you observe?

What will happen if some A is now added?

What will happen to the rates of the reaction immediately after the following changes are made and how will the equilibrium adjust if:
Some A is added?

Some D is added?

Some B is removed?

Some C is removed?

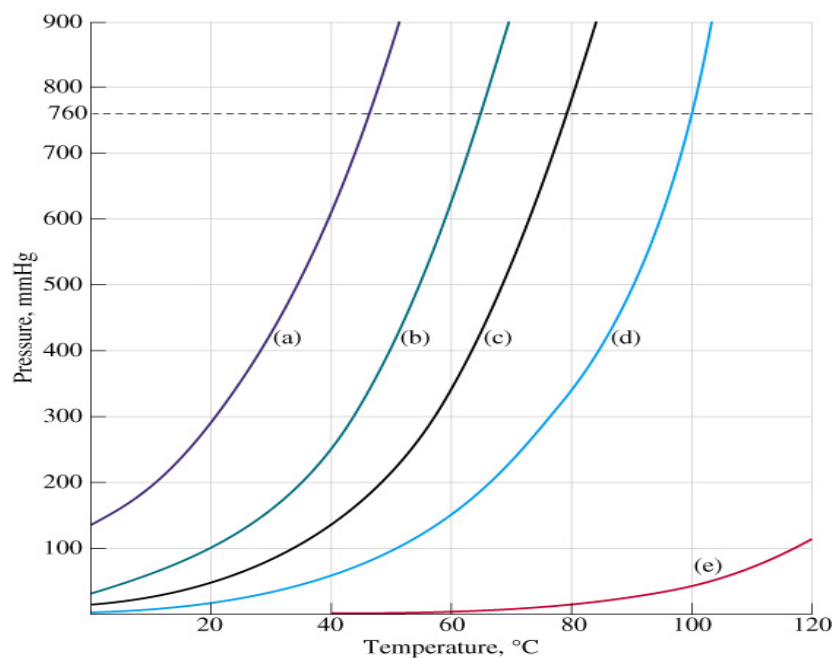
Important Notes:

Equilibrium systems will adjust to get to equilibrium.

If stressed (changed so as to not be in equilibrium), the system will also adjust to return to equilibrium

IB Chemistry — Equilibrium

Phase Equilibrium is an Equilibrium between a liquid and its vapour. The position of this equilibrium is described by the term vapour pressure. This term describes the pressure of the gas above a liquid at equilibrium. The size and shape of the container have no effect on this equilibrium pressure.



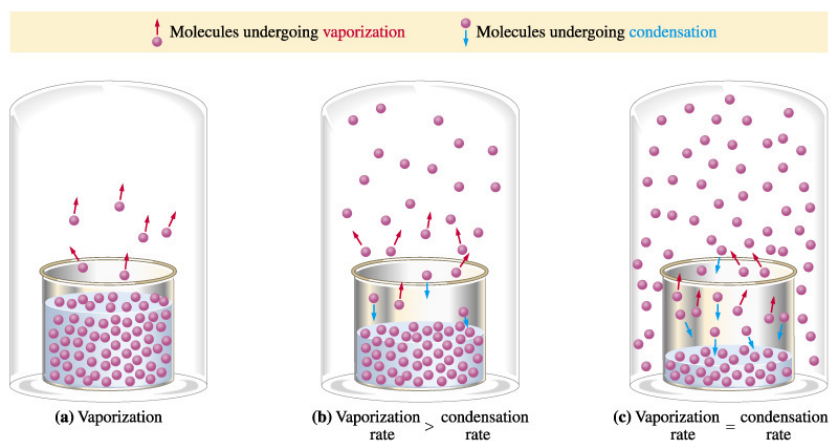
Which curve is water?

What are the boiling points of these liquids?

Why does vapour pressure increase with temperature?

Why does the shape of the container not matter?

This is a diagram of a liquid system reaching equilibrium. Explain each step.



The rate of condensation varies with the concentration of the vapour. The concentration will vary until the rate of condensation equals the rate of vaporization.

p. 432 figure 12.6

For each substance shown on the graph, explain the following processes:

- Each liquid is placed in an evacuated container and reaches equilibrium.
- Each gas is placed in a container and allowed to reach equilibrium.
- Explain differences between the different substances at equilibrium and intermolecular forces.

Follow Up Problems 16.4, 5
Problems 12.13, 14; 17.1, 3

Le Châtelier's Principle

Le Châtelier's Principle allows us to make a prediction about how an Equilibrium system will react to a change.

Stress — A factor that changes that disturbs an equilibrium system

Shift — Reaction to a stress. Shift to right produces more products. Shift to the left produces more reactants.

Le Châtelier's Principle:

A system at equilibrium, subjected to stress, will shift to try and minimize the change that caused the stress.

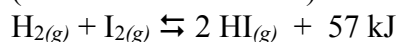
The shift is caused by the forward and reverse rates no longer being equal.

Changes in Concentration

If a species concentration is lowered the equilibrium will shift towards that species to increase its concentration. (Minimize the decrease)

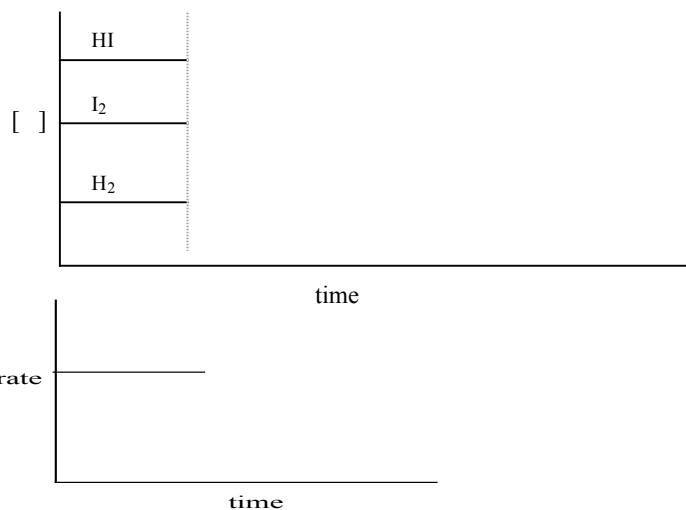
If a species concentration is raised the equilibrium will shift away that species to decrease its concentration. (Minimize the increase)

(Minimize the increase)

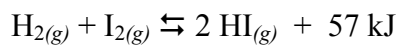


Some H_2 is added to this equilibrium.

How will the equilibrium shift?



IB Chemistry — Equilibrium



Some HI is removed from this equilibrium.

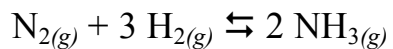
How will the equilibrium shift?



Pressure changes for a gaseous system through a volume change

If the volume of the container is changed, the pressures of the gasses are changed, and the equilibrium will adjust.

The shift will try to minimize the change in pressure.



This reaction at equilibrium has its volume increased:

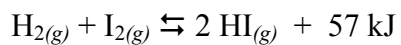
Pressure change?

Shift?

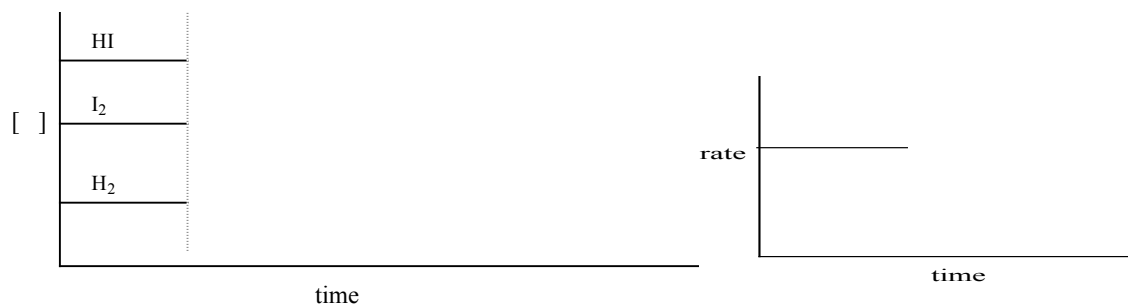
Sketch the concentration and rate graphs

Repeat for a volume decrease.

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The volume of the container is decreased

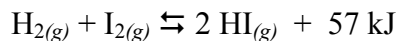


Change in temperature

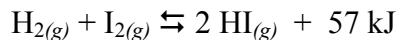
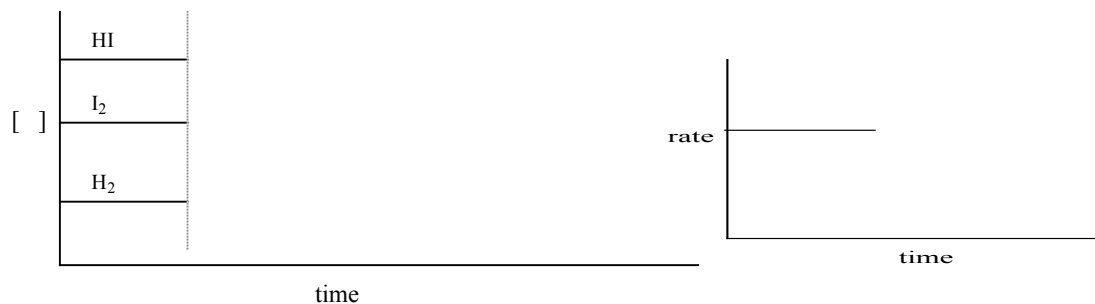
A temperature change has a greater effect on the endothermic reaction.

A temperature increase will cause a shift away from the energy term to consume energy and lower the temperature.

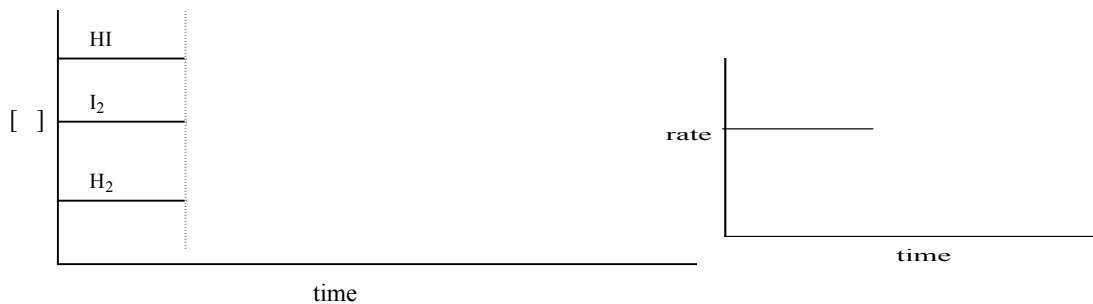
A temperature decrease will cause a shift towards the energy term to produce energy and increase the temperature.



The temperature is decreased.



The temperature is increased.



IB Chemistry — Equilibrium

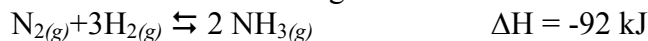
Adding a Catalyst

A catalyst speeds up both the forward and reverse reaction rates equally.

The rates are both increased, but still equal: no shift.

Add an inert gas. This increases the pressure of the system, but not the pressures or concentration of the reactant or products. NO SHIFT.

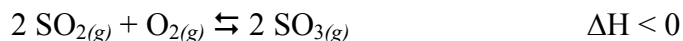
Haber Process for making ammonia



What conditions would favour the production of large amounts of ammonia?

Why is this process run successfully at high pressures and temperatures?

The contact process to make Sulphuric Acid has an equilibrium step in it:



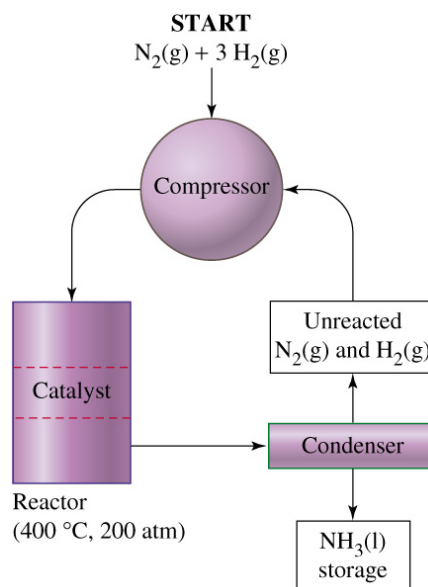
What conditions should be used to maximize yield?

Why is this process done at 1 atm, and high temperature with a catalyst (VO_2)?

Handout: 17-23

Handout: 24-28 Indicate how the forward and reverse rates will be affected for these questions.

Problem 17.99



IB Chemistry — Equilibrium

Mathematical model for Equilibrium:

For: $aA + bB \rightleftharpoons cC + dD$

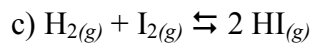
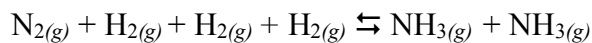
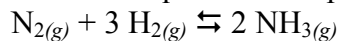
The Equilibrium expression K_{eq} is:

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

If concentrations are used in this expression it is called “ K_c ”

Example 1:

Write the equilibrium expression for:



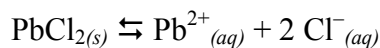
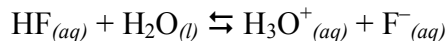
The equilibrium expression deals with concentrations that are variable.

Solids and pure liquids have constant concentrations.

They are omitted from the equilibrium expression.

Example 2:

Write the Equilibrium expression for:



K_{eq} describes a relationship between product and reactants:

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]}$$

The size of the numeric value of K will show if the equilibrium favours reactants or products.

An equilibrium that favours products:

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]} = \frac{\text{large}}{\text{small}} = \text{large \#}$$

An equilibrium that favours reactants:

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]} = \frac{\text{small}}{\text{large}} = \text{small \#}$$

ONLY TEMPERATURE CHANGES WILL AFFECT THE VALUE OF “K”

Changes of pressure or concentration will shift the equilibrium, but they will NOT change the value of “ K ”.

If the temperature changes, we can determine the change in the value of “ K_c ” by using Le Châtelier’s principle.

A shift to the product’s side corresponds with an increase in “ K_c ”.

A shift to the reactant’s side corresponds with a decrease in “ K_c ”.

Example 3:

a) For $A_{(g)} \rightleftharpoons B_{(g)} + \text{Energy}$.

What is the change in “ K_c ” if the temperature is decreased?

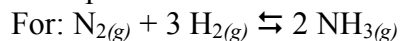
b) An equilibrium has its value of “ K_c ” decrease for a temperature increase. Is the reaction endothermic or exothermic?

IB Chemistry — Equilibrium

Given the concentrations of all species at equilibrium, the value of “ K_c ” can be calculated.

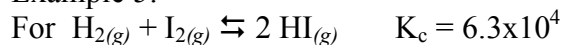
Given the value of “ K_c ” and one unknown species concentration, the unknown can be found.

Example 4:



At equilibrium there are 0.012 mole of ammonia, 1.35 moles of hydrogen, and 1.85 moles of nitrogen in a 5.0 L container. What is the value of the equilibrium constant at this temperature?

Example 5:



The $[\text{HI}] = 2.45 \text{ M}$, and $[\text{I}_2] = 0.023 \text{ M}$. What is the equilibrium concentration of H_2 ?

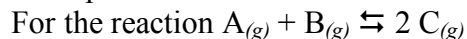
If we must calculate how much a reaction shifts to get to equilibrium, we use an “ICE” Table.

I = initial concentration

C = change in concentration

E = equilibrium concentration.

Example 6:

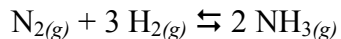


Initially, 1.0 moles of each gas was placed in a 2.0 L container.

At equilibrium, $[\text{C}] = 0.80 \text{ M}$. What is the value of “ K_c ” for this equilibrium?

Example 7:

For the reaction:



1.00M of ammonia was placed in a 1.00 L container. After some time, $[\text{H}_2] = 1.35 \text{ M}$, and was not changing. What is the value of “ K_c ”?

Follow Up Problems 17.3, 8, 9(b)

Problems 17.38, 41, 43, 49, 51, 53, 55

Equilibrium — Calculations

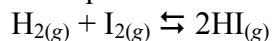
To determine if a system is at equilibrium, we calculate a K_{trial} or a “Q” value and compare it to a known K value.

If $K_{\text{trial}} = K_{\text{eq}}$ then the system is at equilibrium.

If $K_{\text{trial}} < K_{\text{eq}}$ then the system will shift right.

If $K_{\text{trial}} > K_{\text{eq}}$ then the system will shift left.

Example 1:



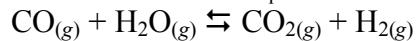
4.00 Moles of HI, 2.00 Moles of H_2 , and 1.75 Moles of I_2 are placed in a 2.0 L reaction flask. $K_{\text{eq}} = 56.0$

Is the reaction at equilibrium? If not, which way will it have to shift to reach equilibrium?

IB Chemistry — Equilibrium

Example 2:

For the reaction: $K_{\text{eq}} = 1.2 \times 10^{-5}$



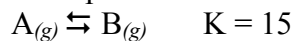
A reaction mixture is found to contain: 3.5 M CO, 5.0 M H₂O, 0.050 M CO₂, and 0.0040 M H₂.

How will the equilibrium shift to reach equilibrium?

Some “ICE” calculations require the use of an unknown in the table.

If we are not given specific information about initial or equilibrium concentrations, we often must use a value “x”, and solve for that value.

Example 3:



0.50 moles of A are placed in a 1.0 L container and allowed to reach equilibrium. What are the concentrations of A and B at equilibrium?

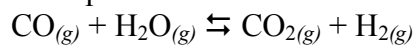
IB Chemistry — Equilibrium

Example 4:



Initially, $[\text{H}_2] = [\text{I}_2] = 0.75 \text{ M}$. The system is allowed to reach equilibrium. What are the concentrations of all species?

Example 5:



This reaction is at equilibrium with 2.00 moles of CO, 2.00 moles of H₂O, 1.00 moles of CO₂, and 3.00 moles of H₂ in a 1.00 L container.

1.00 moles of H₂ is added to the container. What are the new equilibrium concentrations?

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Problems

17.33, 113

Entropy and Enthalpy

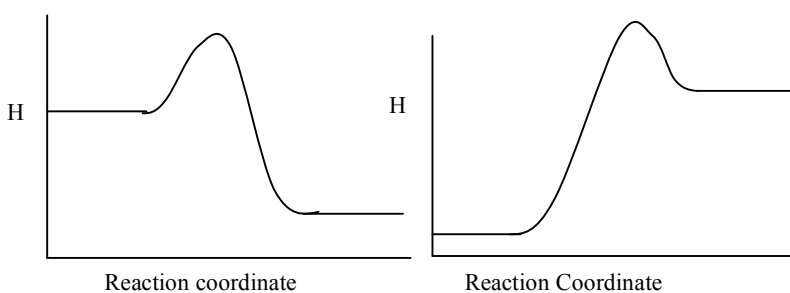
Every reaction has two factors that will determine if it does not react, if it react completely, or if it ends in an equilibrium.

Enthalpy (energy) — A system will tend to minimum potential energy.

Entropy (randomness) — a system will tend to maximum entropy.

Equilibrium — Entropy and Enthalpy

From potential energy diagrams we can see the side favoured by minimum potential energy (Enthalpy “H”)



Entropy (“S”) will favour the side with the most randomness — the most particles in the most random phase.

Greater randomness is favoured because there are more ways to arrange the particles randomly than orderly.

Gasses >> solutions > liquids >> solids

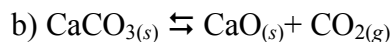
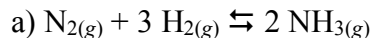
Entropy can be calculated from standard entropy values.

$$\Delta S^\circ = S^\circ_{(\text{products})} - S^\circ_{(\text{reactants})}$$

The values of the standard entropies can be found in the appendix and in your IB Data booklet for some organic compounds.

Example 1:

Estimate and calculate the ΔS for the following:



IB Chemistry — Equilibrium

A system will tend to minimum enthalpy and maximum entropy.
Both factors favour reactants → practically no reaction.
Both factors favour products → practically reacts to completion.
One factor favour reactants and the other products → observable equilibrium.

The tendency for a reaction to proceed can be calculated with a function called Gibb's free (ΔG):

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

If ΔH , ΔS , and the temperature are known, then ΔG can be calculated.

If $\Delta G < 0$ then the reaction is spontaneous.

If $\Delta G > 0$ then the reaction is not spontaneous.

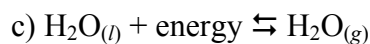
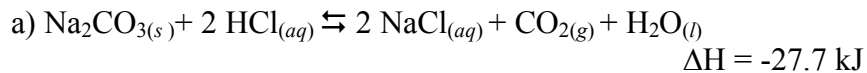
If $\Delta G = 0$ the reaction is at equilibrium.

If the reaction is at standard state (298K, 25°C) then Gibb's free energy can be calculated with:

$$\Delta G^\circ = \Delta G^\circ_{\text{products}} - \Delta G^\circ_{\text{reactants}}$$

Example 2:

Qualitatively, will the following reactions will the reaction not proceed, be in equilibrium, or go to completion? Estimate the sign of ΔG .



IB Chemistry — Equilibrium

Example 3:

For this process:

indicate what happens to spontaneity at high temperatures and low temperatures.

At what temperature will the process be at equilibrium ($\Delta G = 0$)



Follow Up Problems 20.2, 4, 5, 6

Problems 20.5, 10, 12, 16, 18, 33, 35, 48, 50, 52, 54, 83