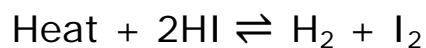




## Dynamic Equilibrium

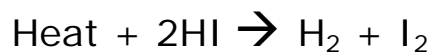
Consider the endothermic reaction for the thermal decomposition of hydrogen iodide: HI



For this reaction to be reversible, the products ( $\text{H}_2 + \text{I}_2$ ) need to remain in the reaction container. Such a system is a *closed system*

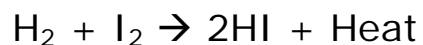
At equilibrium there are two opposing reactions occurring. One is the decomposition reaction of HI into  $\text{H}_2$  and  $\text{I}_2$  and the other is the combination reaction of  $\text{H}_2$  and  $\text{I}_2$  into HI. Only reversible reactions form an equilibrium.

Initially, only the forward reaction occurs as the HI decomposes.



Since there are no products, the reverse rate is zero.

But, as products form during the course of the reaction the concentration of products increases and the reverse reaction begins to occur:



Eventually, the two opposing rates become equal and a state of equilibrium exists:

At this point no further macroscopic (observable) changes occur, although both the forward and reverse reactions are continuing. The concentration of each species remains constant. This is known as the *equilibrium concentration*.

A state of equilibrium is reached by starting either with reactants or with products, and can be attained from either end. The equilibrium state, if upset, will re-establish itself. If additional reactants are introduced, the equilibrium shifts so as to re-establish a new equilibrium. If products are added, the equilibrium re-establishes itself.

Since the forward reaction consumes energy in this example and the reverse reaction produces energy, then, at equilibrium, both rates are equal and the heat consumed equals the heat produced. An equilibrium then exists at *constant temperature*.

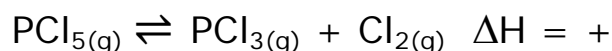
## Recognizing Equilibrium States

A state of equilibrium exists whenever:

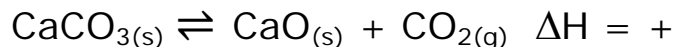
1. There is a closed system
2. The reaction is reversible
3. There is a constancy in macroscopic properties
4. The temperature remains constant

Look for a property that can be monitored. When this property remains constant, a state of equilibrium exists.

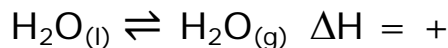
Ex. What property might be monitored in order to establish if a state of equilibrium exists?



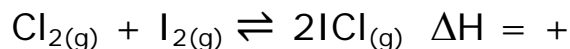
**Comment:** as the forward reaction proceeds, pressure increases



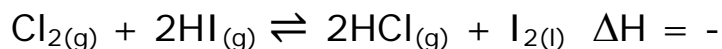
**Comment:** as the forward reaction proceeds, pressure increases



**Comment:** as the forward reaction proceeds, pressure increases



**Comment:** Iodine has a purple colour. Note that the pressure remains constant during the reaction.



**Comment:** Iodine has a purple colour and as the reaction proceeds forward, the pressure will decrease

## Factors Controlling the Equilibrium

There are two driving factors for all chemical processes:

### A. A tendency to achieve a lower heat content ( $\Delta H$ )

Enthalpy drive is towards the *lower thermal energy*.

#### 1. Exothermic Reactions

*Reactants have a high heat content* → *Products have a low heat content* + Heat

For an exothermic reaction the enthalpy drive is towards the PRODUCTS →

#### 2. Endothermic Reactions

*Reactants have a low heat content* + Heat → *Products have a high heat content*

For an endothermic reaction the enthalpy drive is towards the REACTANTS ←

### B. A tendency to achieve a higher state of disorder ( $\Delta S$ )

Entropy drive is towards the side with *more disorder*.

**Gases** (Highest entropy, most random)

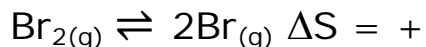
**Aqueous Ions** (very high disorder, but lower in energy)

**Liquid** (medium order, medium energy)

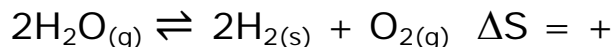
**Solid** (low energy and highly ordered)

Within the same phase an *increase in the total number of particles* indicates an increase in entropy

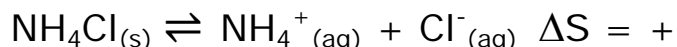
## 1. Estimating the change in Entropy (S)



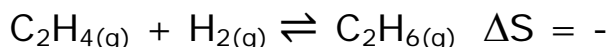
**Comment:** entropy favours free atoms (non-bonded)



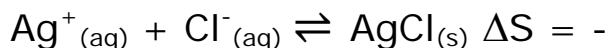
**Comment:** entropy favours greater number of particles



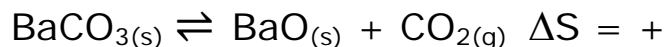
**Comment:** entropy favours ions



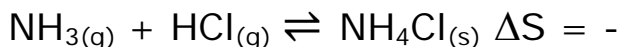
**Comment:** entropy favours greater number of particles



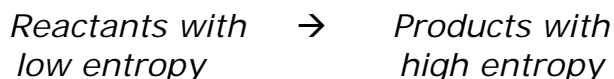
**Comment:** entropy favours ions



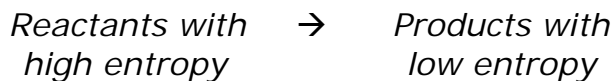
**Comment:** entropy favours gas



**Comment:** entropy favours gas



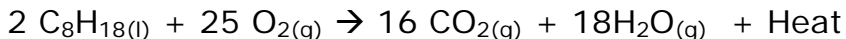
- When the entropy increases, the **PRODUCTS** are favoured. The entropy drive is to the right  $\rightarrow$



When the entropy increases, the **REACTANTS** are favoured. The entropy drive is to the left  $\leftarrow$

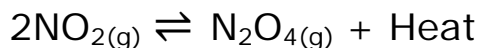
Equilibrium does **NOT EXIST** when both factors favour the formation of products: such as an exothermic reaction with increasing entropy.

This is called **A SPONTANEOUS REACTION**



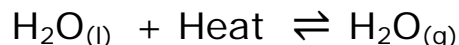
Reactions don't exist in which both factors favor the formation of reactants. **NO REACTION**

- When both factors favour opposing sides (one favours products, the other favours reactants) then there is a *reversible reaction*. Such reactions form equilibria. These equilibria can be shifted forward or backward.



**Comment:** *the enthalpy drive favours products. The entropy drive favours reactants.*

The factor which accounts for the forward reaction is the ENTHALPY drive. The factor which accounts for the reverse reaction is the ENTROPY drive



**Comment:** *the enthalpy drive favours reactants. The entropy drive favours products.*

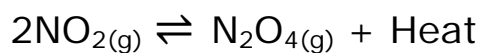
The factor which accounts for the forward reaction is the ENTROPY drive. The factor which accounts for the reverse reaction is the ENTHALPY drive

## Factors affecting Equilibrium

An equilibrium can be shifted forward or backward by a variety of changes to its conditions.

### A. Concentration

Increasing the concentration of a species in an equilibrium increases its collision frequency and its rate of reaction. The equilibrium then favours the formation of this specie's products: the equilibrium shifts away from the increased concentration.

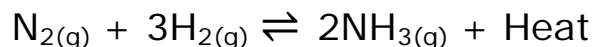


Adding  $\text{NO}_2$  shifts the equilibrium toward the product side, producing additional  $\text{N}_2\text{O}_4$ .



## B. Volume and Pressure

Decreasing the volume of a container increases the collision frequency of both FWD and REV rates. If there are more gas molecules of the reactants than products in the reaction equation, the equilibrium shifts so as to reduce the number of gas molecules.



Reducing the volume shifts the equilibrium toward the product side (because of less particles) producing additional  $\text{NH}_3$

### Pressure

- Increasing the pressure by *decreasing* the volume is similar to above.
- Increasing the pressure by adding a reactant is similar to conc change.
- Increasing the pressure by adding an inert gas (non-reactant) has no effect, because the change in pressure affects all reactants equally.

### C. Temperature

Increasing the temperature will increase both the forward reaction rate and the reverse reaction rate. However, the ENDOTHERMIC rate will increase more than the exothermic rate, hence the endothermic reaction is favored and the equilibrium shifts away from the heat term.

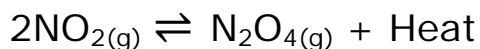


Adding heat (raising the temperature) favours the endothermic reaction and shifts the equilibrium toward the product side, producing additional  $\text{H}_2\text{O}_{(g)}$

### D. Catalyst

A catalyst increases only the rates. Both rates increase equally. There is no change in the equilibrium.

Ex. Consider the reaction:



What effect will each change have on the amount of  $\text{N}_2\text{O}_{4(g)}$

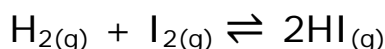
1. Decrease temperature
2. Increase volume
3. Add more  $\text{NO}_2$
4. Add He gas
5. Remove some  $\text{NO}_2$
6. Decrease pressure by changing volume
7. Decrease volume by changing pressure
8. Add some heat

## Le Chatelier's Principle

*Whenever a stress is applied to a system at equilibrium, the system will respond so as to reduce the stress.*

### A. Concentration

If H<sub>2</sub> is added to the equilibrium



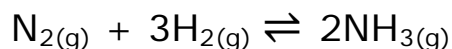
The stress is the increase in [H<sub>2</sub>]

The equilibrium shifts away from the stress, H<sub>2</sub>

The products are favoured. →

### B. Volume and Pressure

If volume is decreased



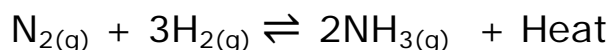
The stress is decreased space, or too many molecules

The equilibrium shifts away from the stress towards less molecules

The products are favoured. →

### C. Temperature

If the temperature is decreased



The stress is too little heat

The equilibrium shifts to produce more heat

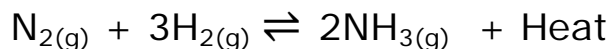
The products are favoured. →

### D. Catalyst

Have no effect on equilibrium. Affects both FWD and REV reaction rates equally.

## Applications of Equilibrium

Haber Process



Just prior to World War 1, Germany was dependent on sodium nitrate and guano sources from Chile; for nitrogen containing compounds needed to make explosives and fertilizers. The British navy blockaded the coast line and these shipments were stopped. German Chemist Fritz Haber (1868 - 1934) (Also chemist Walther Nernst and engineer Kurt Bosch) examined this reaction and applied the principles of equilibria to increase the yield of ammonia to levels that made this process viable. He:

Pressure: Increased to 200 times atmospheric pressure

Temperature: Increase to improve rate  
Decrease to favour products  
Generally 700-900 K (middle temp)

Catalyst: Haber used Os at first – rare and expensive  
Finally used a mixture of iron oxides and Al

Also removed ammonia as it was produced by liquification and the N<sub>2</sub> and H<sub>2</sub> are recycled.

This enabled Germany to continue production of explosives despite the blockade. Haber also developed the use of chlorine gas as a weapon. In 1918, amidst much controversy, he was awarded the Nobel Prize for chemistry. Ironically, in 1933 he was expelled from Germany by the Nazis because he was Jewish. He died shortly afterwards in 1934. Today there are several hundred ammonia plants around the world which use the Haber process.

True story

## Quantitative Equilibrium

### The Equilibrium Constant

For any reversible reaction  $A + B \rightleftharpoons C + D$  at equilibrium, the forward rate = reverse rate

Then there is a constant ratio between the equilibrium concentrations of the products and that of the reactants.

$$K_{\text{eq}} = \frac{[C] \times [D]}{[A] \times [B]}$$

Where  $K_{\text{eq}}$  is the *equilibrium constant*.

For the reaction:  $3A + B \rightleftharpoons 2C + D$

The equation could be thought of as:  $A + A + A + B \rightleftharpoons C + C + D$

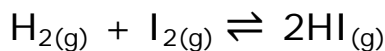
And the equilibrium expression would be

$$K_{\text{eq}} = \frac{[C][C][D]}{[A][A][A][B]}$$

Which can be simplified to:

$$K_{\text{eq}} = \frac{[C]^2 \times [D]}{[A]^3 [B]}$$

Ex. Write an equilibrium constant expression for hydrogen gas and iodine gas reacting to form hydrogen iodide gas.



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

## Equilibrium Expression rules

1. All gases, aqueous ions and mixtures of liquids are included in the expression
2. All *solids* and *pure liquids* (usually water) are never included.

## Interpreting $K_{eq}$ Values

### Effect of Equilibrium Factors

1. **Catalysts, concentration, volume and pressure** *do not affect the constant*. That is why it is a CONSTANT! Changing any one of these factors simply causes an equilibrium shift to restore the equilibrium and return to the original ratio between products and reactants.
2. **Temperature** *affects the constant*. When the temperature increases the rates increase. However, the endothermic rate increases more quickly than the exothermic rate, hence the ratio of products to reactants changes. At a different temperature the amounts of products and reactants is different from what they were initially.

### Use Le Chatelier's principle to determine the result

For an *exothermic* reaction, increasing the temperature favours reactants. Hence  $K_{eq}$  will decrease.

For an *endothermic* reaction, increasing the temperature favours products. Hence  $K_{eq}$  will increase.

### Effect of equation style

For the equation:  $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

The  $K_{eq}$  expression is: 
$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = 50.2$$

But if you were to write the equation:  $\frac{1}{2} H_{2(g)} + \frac{1}{2} I_{2(g)} \rightleftharpoons HI_{(g)}$

The  $K_{eq}$  expression becomes: 
$$K_{eq} = \frac{[HI]}{[H_2]^{\frac{1}{2}}[I_2]^{\frac{1}{2}}} = 7.09$$

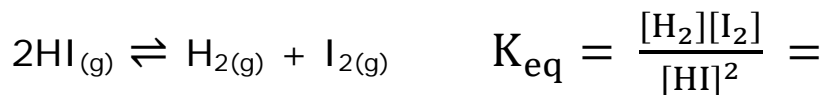
Since the equilibrium expression for the second equation is simply the square root of the first, then the value of  $K_{\text{eq}}$  for the second must be the square root of the first;

$$K_{\text{eq}} = \sqrt{50.2} = 7.09$$

Generally, doubling an equation squares the original constant, and halving the equation produces a constant that is the root of the original one.

### Effect of Reversing the Equation

Reversing an equation inverts the equilibrium expression. The new  $K_{\text{eq}}$  will then be the reciprocal of the original constant.



### Relative Constant Interpretation

Since the  $K_{\text{eq}}$  represents the ratio between equilibrium concentrations of products to reactants, then:

Large ( $>1$ )  $K_{\text{eq}}$  means products favoured.

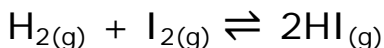
Small ( $<1$ )  $K_{\text{eq}}$  means reactants favoured.

But only when similar equation styles are compared.

## More Math (Applications)

### Calculating the Equilibrium Constant (AT EQUILIBRIUM)

Consider the following equilibrium:



Find the value of  $K_{\text{eq}}$  if

$$\begin{aligned} [\text{H}_2] &= 0.46 \text{ M} \\ [\text{I}_2] &= 0.39 \text{ M} \\ [\text{HI}] &= 3.0 \text{ M} \end{aligned}$$

Substitute equilibrium concentrations from last line into equilibrium expression and solve for  $K_{\text{eq}}$ .

### Calculating the Equilibrium Constant (NOT AT EQUILIBRIUM)

Consider the following equilibrium:  $\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$

Find  $K_{\text{eq}}$  if the

$$\begin{aligned} \text{initial } [\text{PCl}_5] &= 0.70\text{M (and no other initial chemicals)} \\ \text{Final } [\text{Cl}_2] &= 0.15\text{M} \end{aligned}$$

When you have a system that is NOT at equilibrium, and you need to find out the  $K_{\text{eq}}$  (or other concentrations) we need to set up a working table listing species and concentrations, generally called a RICE table

Reaction	$\text{PCl}_5 \rightleftharpoons$	$\text{PCl}_3 +$	$\text{Cl}_2$
[Initial]	0.70	0.00	0.00
Change			
[Equilibrium]			0.15



### Calculating Equilibrium [ ] (only some Eq<sup>m</sup> [ ]'s given) - Easy

Consider the equilibrium:  $\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$   $K_{\text{eq}} = 50.2$

Find equilibrium concentration of HI if at equilibrium:

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

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

Reaction	$\text{H}_2$	+	$\text{I}_2$	$\rightleftharpoons$	$2\text{HI}_{(g)}$
[Initial]	-		-		-
Change	-		-		-
[Equilibrium]	0.50		0.50		<b>X</b>

### Calculating Equilibrium [ ] (only initial [ ]'s given) - Harder

Consider the equilibrium:  $\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$   $K_{\text{eq}} = 50.2$

What are the Eq<sup>m</sup> [ ]'s of each substance if initially only have:

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

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

Reaction	$\text{H}_2$	+	$\text{I}_2$	$\rightleftharpoons$	$2\text{HI}_{(g)}$
[Initial]	0.50		0.50		
Change					
[Equilibrium]					

### Calculating Equilibrium [ ] (only initial [ ]'s given) - Hardest

Consider the equilibrium:  $\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$   $K_{\text{eq}} = 50.2$

What are the Eq<sup>m</sup> [ ]'s of each substance if a 0.50L flask contains:

2.0 mol of  $\text{H}_2$

1.0 mol of  $\text{I}_2$

AND at a later time 1.0 mol of  $\text{I}_2$  are added.

Reaction	$\text{H}_2$	+	$\text{I}_2$	$\rightleftharpoons$	$2\text{HI}_{(g)}$
[Initial]	4.0		2.0		0.00
<b>ADDED</b>			<b>2.0</b>		
Change					
[Equilibrium]					

## Calculating the Equilibrium constant

Consider the equilibrium:  $2\text{NH}_3(\text{g}) \rightleftharpoons 3\text{H}_2(\text{g}) + \text{N}_2(\text{g})$

Initially a 5.0L flask contains only:

1.0 mol of  $\text{NH}_3$  and  
0.40 mol of  $\text{N}_2$

After equilibrium is established, 0.78 mol  $\text{NH}_3$  remain. Find the value of  $K_{\text{eq}}$

Reaction	$2\text{NH}_3(\text{g}) \rightleftharpoons$	$3\text{H}_2$	+	$\text{N}_2(\text{g})$
[Initial]	0.20			0.080
Change				
[Equilibrium]	0.156			