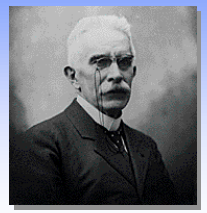
## EQUILIBRIUM AND EXTERNAL EFFECTS

- Temperature, catalysts, and changes in concentration affect equilibria.
- The outcome is governed by **LE CHATELIER'S PRINCIPLE**
- "...if a system at equilibrium is disturbed, the system tends to shift its equilibrium position to counter the effect of the disturbance."

## EQUILIBRIUM AND EXTERNAL EFFECTS



Henri Le Chatelier
1850-1936
Studied mining engineering.
Interested in glass and ceramics.

## EQUILIBRIUM AND EXTERNAL EFFECTS

- Temperature change ---> change in K
- Consider the fizz in a soft drink
  $CO_2(g) + H_2O(liq)$ ⇌ $CO_2(aq)$ + heat
- Decrease T. What happens to equilibrium position? To value of K?
- $K = [CO_2] / P(CO_2)$
  K increases as T goes down because $[CO_2]$ increases and $P(CO_2)$ decreases.
- Increase T. Now what?
- Equilibrium shifts left and K decreases.

## Temperature Effects on Equilibrium

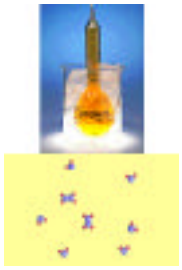
$N_2O_4$ (colorless) + heat ⇌ 2 $NO_2$ (brown)

$\Delta H^o = +57.2$ kJ

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

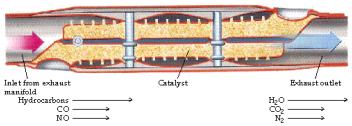
$K_c$ (273 K) = 0.00077

$K_c$ (298 K) = 0.0059

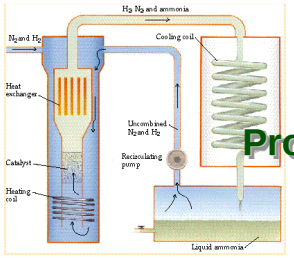


## EQUILIBRIUM AND EXTERNAL EFFECTS

- Add catalyst ---> no change in K
- A catalyst only affects the RATE of approach to equilibrium.




Catalytic exhaust system




## $NH_3$ Production

- $N_2(g) + 3\ H_2(g)$ ⇌ $2\ NH_3(g)$
- $K = 3.5 \times 10^8$ at 298 K

## EQUILIBRIUM AND EXTERNAL EFFECTS

- Concentration changes ---> no change in K — only the position of equilibrium changes.

## Le Chatelier's Principle

Adding a "reactant" to a chemical system.

## Le Chatelier's Principle

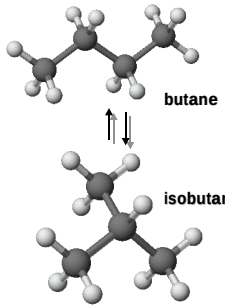
Removing a "reactant" from a chemical system.

## Le Chatelier's Principle

Adding a "product" to a chemical system.

## Le Chatelier's Principle

Removing a "product" from a chemical system.

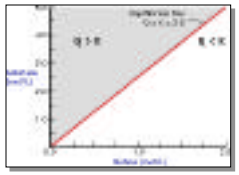


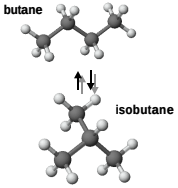

## Butane-Isobutane Equilibrium

$$K = \frac{[\text{isobutane}]}{[\text{butane}]} = 2.5$$

## Butane ⇌ Isobutane

Assume you are at equilibrium with [iso] = 1.25 M and [butane] = 0.50 M. Now add 1.50 M butane. When the system comes to equilibrium again, what are [iso] and [butane]? K = 2.5



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Assume you are at equilibrium with [iso] = 1.25 M and [butane] = 0.50 M. Now add 1.50 M butane. When the system comes to equilibrium again, what are [iso] and [butane]? K = 2.5

**Solution**

Calculate Q immediately after adding more butane and compare with K.

$$Q = \frac{[\text{isobutane}]}{[\text{butane}]} = \frac{1.25}{0.50 + 1.50} = 0.63$$

Q is LESS THAN K. Therefore, the reaction will shift to the _____.

## Butane ⇌ Isobutane

You are at equilibrium with [iso] = 1.25 M and [butane] = 0.50 M. Now add 1.50 M butane.

**Solution**

Q is less than K, so equilibrium shifts right — away from butane and toward isobutane.

Set up concentration table

| | [butane] | [isobutane] |
|---|---|---|
| Initial | 0.50 + 1.50 | 1.25 |
| Change | - x | + x |
| Equilibrium | 2.00 - x | 1.25 + x |

## Butane ⇌ Isobutane

You are at equilibrium with [iso] = 1.25 M and [butane] = 0.50 M. Now add 1.50 M butane.

**Solution**

$$K = 2.50 = \frac{[\text{isobutane}]}{[\text{butane}]} = \frac{1.25 + x}{2.00 - x}$$

x = 1.07 M

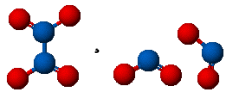
At the new equilibrium position,

[butane] = 0.93 M and [isobutane] = 2.32 M.

Equilibrium has shifted toward isobutane.

## Nitrogen Dioxide Equilibrium

$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$



$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.0059 \text{ at } 298 \text{ K}$$

Increase P in the system by reducing the volume.

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Increase P in the system by reducing the volume.

In gaseous system the equilibrium will shift to the side with fewer molecules (in order to reduce the P).

Therefore, reaction shifts LEFT and P of $NO_2$ decreases and P of $N_2O_4$ increases.