Today's Topics

- $N_2O_4 \leftrightarrows NO_2$ equilibrium P= (n/V).RT
- Le Chatelier's Principle

Nitrogen Dioxide Equilibrium

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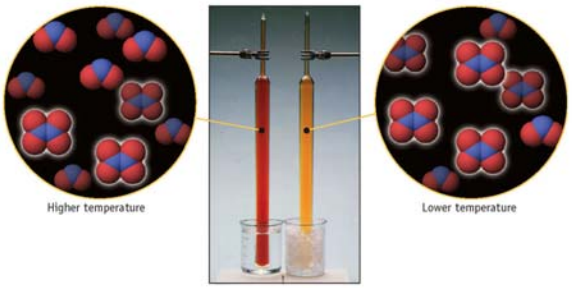
$N_2O_4(g) \leftrightarrows 2\ NO_2(g)$
(colorless) (brown)



Writing and Manipulating K Expressions

Concentration Units

We have been writing K in terms of mol/L.

These are designated by K_c

But with gases, P = (n/V)•RT = [conc]•RT

P is proportional to concentration, so we can write K in terms of P.
These are designated by K_p.

For $H_2(g) + I_2(g) \leftrightarrows 2\ HI(g)$ $K_p = \frac{P^2_{HI}}{P_{H_2}P_{I_2}}$

K_c and K_p may or may not be the same.

Writing and Manipulating K Expressions

K using concentration and pressure units

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

where Δn is the change in the number of moles of gas during the reaction

For $S(s) + O_2(g) \leftrightarrows SO_2(g)$ n Prod 1 − n React 1 = 0

$\Delta n = 0$ and $K_p = K_c$

For $SO_2(g) + 1/2\ O_2(g) \leftrightarrows SO_3(g)$ n Prod 1 − n ReaT 1 + ½ = −½

$\Delta n = -1/2$ and $K_p = K_c(RT)^{-1/2}$

Δn = nProd − nReact

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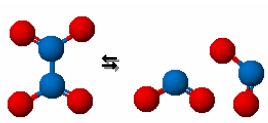
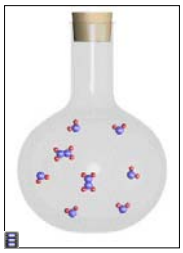
Nitrogen Dioxide Equilibrium

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





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

Increase P in the system by reducing the volume (at constant T).

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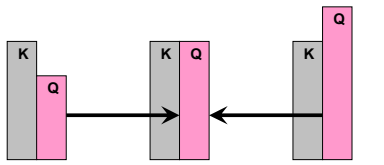
$aA + bB \rightleftharpoons cC + dD$



$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ at any Time K → only at the equilibrium

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Nitrogen Dioxide Equilibrium
$N_2O_4(g) \leftrightarrows 2\ NO_2(g)$

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

Increase P in the system by reducing the volume.

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.

↑ P ⇒ Reduce nber molecules ←

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Nitrogen Dioxide Equilibrium
$N_2O_4(g) \leftrightarrows 2\ NO_2(g)$

N_2O_4 + heat ⇆ 2 NO_2 ΔH^o = + 57.2 kJ

(colorless) (brown)

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

K_c (273 K) = 0.00077

K_c (298 K) = 0.0059

$\Delta H^o > 0$ endothermic

$\Delta H^o < 0$ exothermic

(from Chapter 6)

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Nitrogen Dioxide Equilibrium
$N_2O_4(g) \leftrightarrows 2\ NO_2(g)$

For This reaction

- ΔH^o = + 57.2 kJ (endothermic)
- Increase T. What happens to equilibrium position and the value of K? ?
  K increases as T goes up.
- Decrease T. Now what?
  Equilibrium shifts left and K decreases.

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EQUILIBRIUM AND EXTERNAL EFFECTS

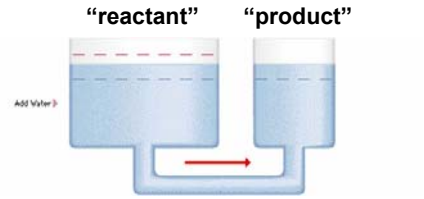
- Temperature and concentration changes affect equilibria.
- The outcome is governed by
  LE CHATELIER'S PRINCIPLE
- "...if a system at equilibrium is disturbed, the system tends to shift its equilibrium position to counter the effect of the disturbance."

Le Chatelier's Principle

- **Change T**
  Changes the value of K
  This causes a change in equilibrium concentrations
- **Add or take away reactant or product:**
  K does not change
  Reaction adjusts to new equilibrium "position"
- **Use a catalyst:**
  K does not change. A catalyst does not affect equilibrium.
  Modify the kinetics of the reaction. (Chapter 15)

Le Chatelier's Principle

"reactant" "product"



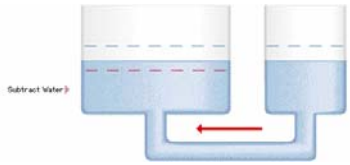
Adding a "reactant" to a chemical system.

reactants ⇆ products

Blue line= initial state
Red line = new state
Water level= eq. state

Le Chatelier's Principle

"reactant" "product"



Removing a "reactant" from a chemical system.

reactants ⇆ products

Blue line= initial state
Red line = new state
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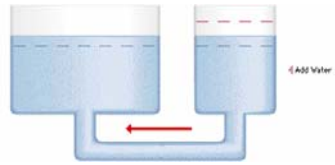
Le Chatelier's Principle

"reactant" "product"



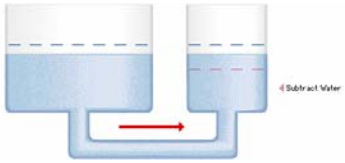
Adding a "product" to a chemical system.

reactants ⇆ products

Blue line= initial state
Red line = new state
Water level= eq. state

Le Chatelier's Principle

"reactant" "product"



Removing a "product" from a chemical system.

reactants ⇆ products

Blue line= initial state
Red line = new state
Water level= eq. state

EQUILIBRIUM AND EXTERNAL EFFECTS

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- Concentration changes:
  - no change in K
  - only the equilibrium composition changes.

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CATALYSIS

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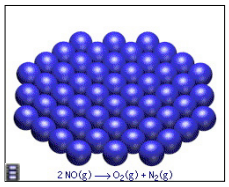
In auto exhaust systems — Pt, NiO

$2\,CO + O_2 \text{ ---> } 2\,CO_2$
$2\,NO \text{ ---> } N_2 + O_2$



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EQUILIBRIUM AND EXTERNAL EFFECTS

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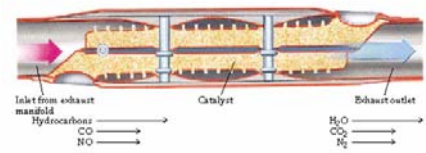

Catalytic exhaust system

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

Rate = $M\,sec^{-1} \equiv M/sec$

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