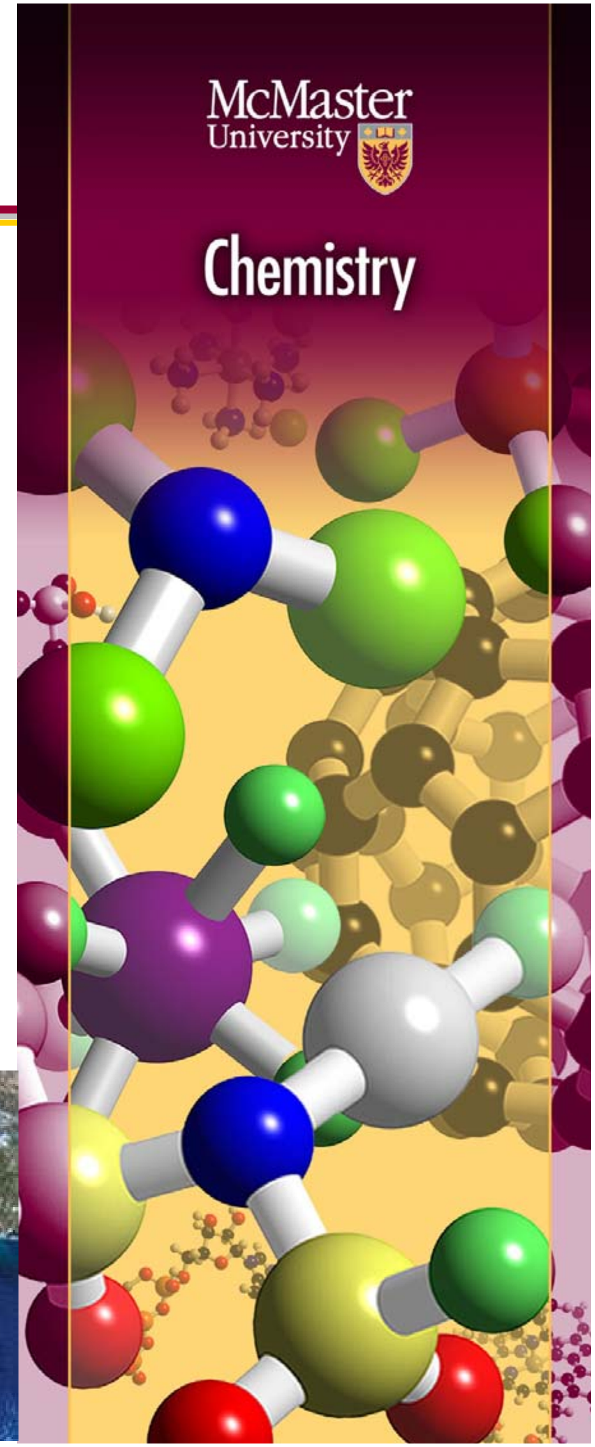
# CHEM 1A03: Intro. Chemistry I

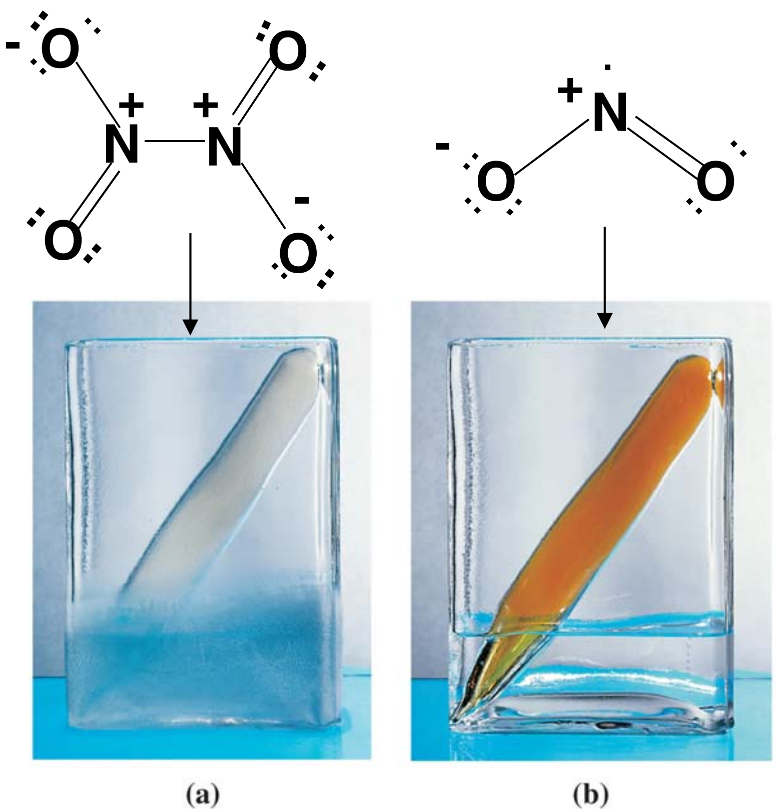
## Dynamic Chemical Equilibrium

*Ch.15: Principles of Chemical Equilibrium*



# Dimerization of Nitrogen Dioxide

$$N_2O_4\,(g) \overset{K}{\rightleftharpoons} 2NO_2\,(g)$$






- **At low T, we have mostly $N_2O_4$**
- **At high T, we have mostly $NO_2$**
- **In general, we have a mixture of the two gases**

# Equilibrium Constant (*K*)

- *K* is a thermodynamic parameter characterizing the tendency for a chemical reaction or process to occur
- Chemical processes are reversible - the extent of reaction (amount of product formed - yield) is determined by *K*
- *K* is a ratio of product to reactant activities, *a* (effective concentration or pressure) at equilibrium – the form of *K* depends on the balanced chemical equation

**General Reaction in Aqueous Solution:**

*Function of T, P, pH etc.* → $K$

$$mA\,(aq) + nB\,(aq) \overset{K}{\rightleftharpoons} xC\,(aq) + yD\,(aq)$$

$$\boxed{K = \frac{a_C{}^{x} a_D{}^{y}}{a_A{}^{m} a_B{}^{n}}}$$

Ch. 15-1, 15-2, p. 658-661 (623-626, 9th ed.)

# Activity

- The activity ($a$) of a solute S is given by

$$a = \gamma\,[S] / [S]_o \qquad \text{we use} \qquad a = [S] \text{ (no units)}$$

where $[S]_o = 1$ mol $L^{-1}$ is the reference state

$\gamma$ is the activity coefficient; assume $\gamma = 1$

$\gamma \approx 1$ under "ideal" conditions (dilute solutions of < 0.001 M)

- The activity ($a$) of a gas, G, is given by

$$a = \gamma\,P_G / P_o \qquad \text{we use} \qquad a = P_G \text{ (no units)}$$

where $P_o = 1$ atm is the reference state; assume $\gamma = 1$

- The activity ($a$) of a pure solid or liquid is 1

  This means we can ignore pure solids or liquids when setting up the equilibrium constant

Ch. 15-2, p. 660-662 (626-628, 9th ed.)

# Activity & Equilibrium Concentrations

- Example: Dissolution of $CaCO_3(s)$

**a = 1**

$$\textit{Pure solid} \rightarrow \quad \underset{}{\overset{a\,=\,1}{CaCO_3\,(s)}} \overset{K_{sp}}{\rightleftharpoons} CO_3^{2-}\,(aq) + Ca^{2+}\,(aq)$$

$$K_{sp} = [CO_3^{2-}]\,[Ca^{2+}] \longleftarrow$$ **Concentrations at eqm**

.

***K appears as unitless because all pressures and concentrations are relative to reference values***

Ch. 15-2; 15-3, p. 667-668 (633-634, 9th ed.)

# $K$ *vs* $K_c$ and $K_p$

- We reserve the subscript on $K$ to denote the type of reaction – e.g. $K_{sp}$ for dissolution reactions (see slide 5)
- $K$ expression may include concentrations (aqueous species) and/or pressures (gases)

e.g. $Zn(s) + 2HCl(aq) \rightleftharpoons ZnCl_2(aq) + H_2(g)$

$$K = \frac{\frac{[[ZnCl_2]}{1mol.L^{-1}} \times \frac{P_{H_2}}{1atm}}{\left[\frac{[HCl]}{1mol.L^{-1}}\right]^2}$$

**Note: for K, all reagents are in their STANDARD STATES:**
**Gases – in Pressures (atm)**
**Solutions – in Concentration (mol/L)**

*We will use "K". In the textbook you will see:*

- $K_C$ when activities are concentrations
- $K_P$ when activities are partial pressures

# Reaction Quotient, *Q*

- $K$ = ratio of products to reactants at **equilibrium**
  (a **constant** at a given temperature, $T$)

- $Q$ = ratio of products to reactants at **any instant**
  (not a constant, can hold any value)

- Relative magnitudes of $Q$ to $K$ determines which direction a reaction will proceed – specifically, ...
- Reaction proceeds
  - in the forward direction, if $Q < K$,
  - in the reverse direction, if $Q > K$

# Chemistry & Dynamic Equilibrium

## Reaction Quotient & Direction of Equilibrium

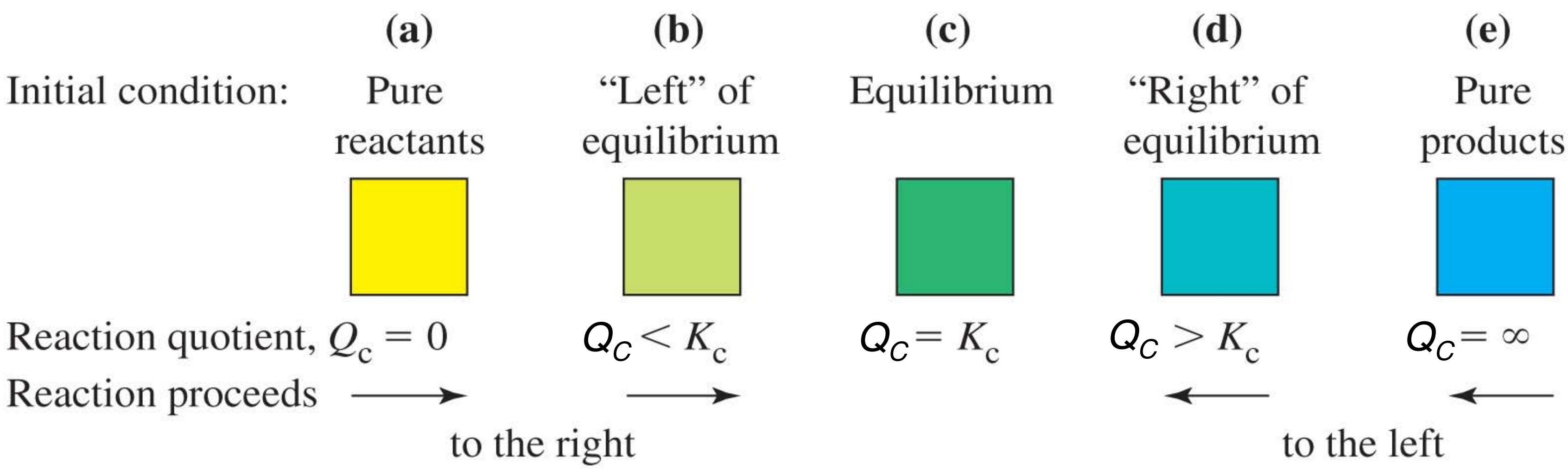





**Fig. 15-5, p. 672 (637, 9th ed.)**

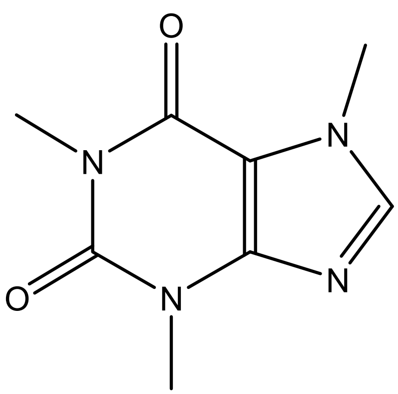
# Octanol-Water Partition Coefficient

## $K_{ow}$ & log $K_{ow}$

- $K_{ow}$ is the octanol-water partition coefficient and gives a measure of lipophilicity of solute (S) molecule
- Large $K_{ow}$ = highly lipophilic

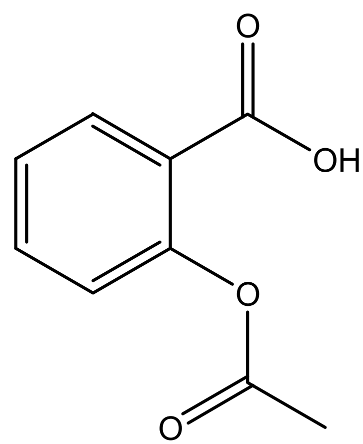
$$\mathrm{S\,(aq)} \underset{}{\overset{K_{ow}}{\rightleftharpoons}} \mathrm{S\,(org)}$$

**Caffeine**



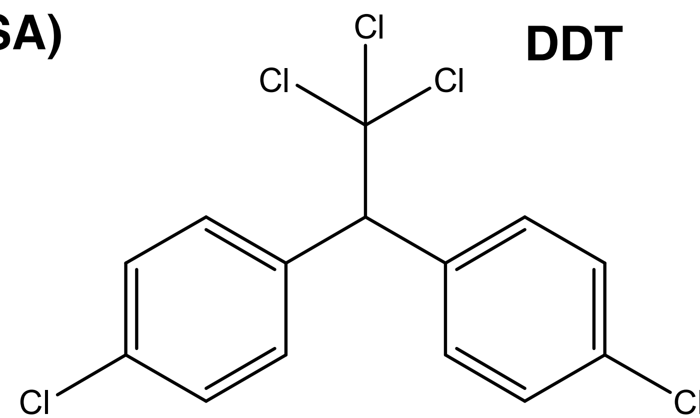

***$K_{ow}$ = 0.85***
***log $K_{ow}$ = -0.07***

**Acetylsalicylic Acid (ASA)**




***$K_{ow}$ = 15.5***
***log $K_{ow}$ = 1.19***

**DDT**




***$K_{ow}$ = 5.0 x $10^6$***
***log $K_{ow}$ = 6.7***

# Persistent Organic Pollutants (POPs)

## Three Characteristics of POPs

1. Persistent: Resist chemical/biochemical transformation

2. Toxic: Acute and/or chronic toxicity (*e.g.,* carcinogenic)

3. Bioaccumulation/Biomagnification: Concentration in fatty tissue that is amplified up the food chain with high log $K_{ow}$

**log $K_{ow}$** is used:

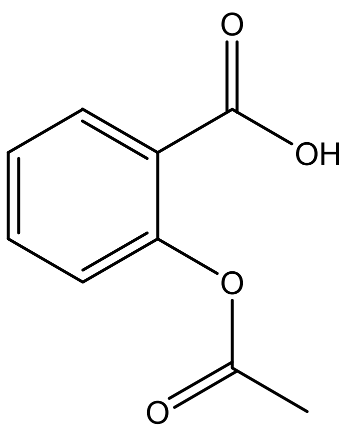
- as a measure of a pollutant's intrinsic "lipophilicity" or "hydrophobicity" (Fat-loving/Water-fearing properties)

- to assess drug toxicity in medicinal chemistry, as pharmaceuticals with log $K_{ow} > 4$ have slow metabolism / elimination

# I-clicker Question #1

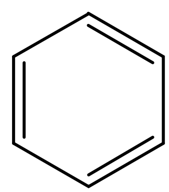
## Octanol-Water Partition Coefficient: log $K_{ow}$

Which chemical is the most lipophilic and has the greatest tendency for bioaccumulation?



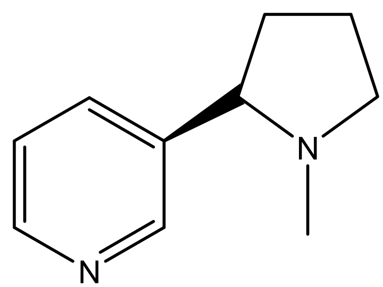
**(a) ASA**

**log $K_{ow}$ = 1.19**



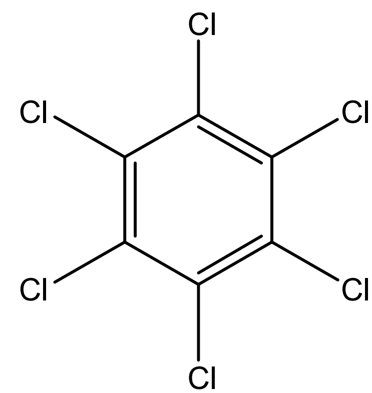
**(b) Benzene**

**log $K_{ow}$ = 2.1**



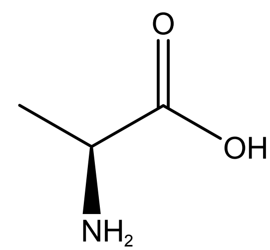
**(c) Nicotine**

**log $K_{ow}$ = 1.17**



**(d) Hexachlorobenzene**

**log $K_{ow}$ = 5.73**



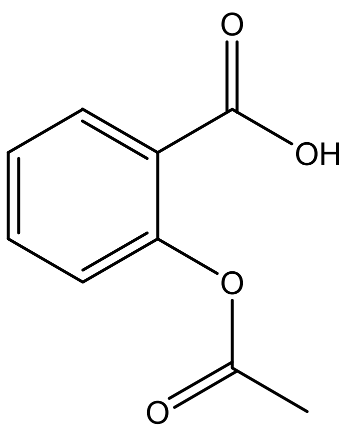
**(e) Alanine**

**log $K_{ow}$ = – 2.16**

# I-clicker Question # 2

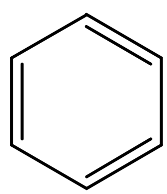
## Octanol-Water Partition Coefficient: log $K_{ow}$

Which chemical is the least lipophilic and has the lowest tendency for bioaccumulation?



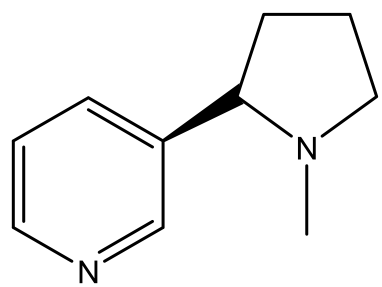
**(a) ASA**

**log $K_{ow}$ = 1.19**



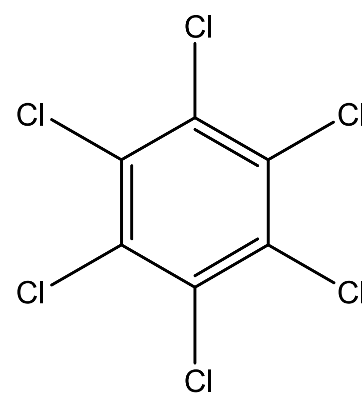
**(b) Benzene**

**log $K_{ow}$ = 2.1**



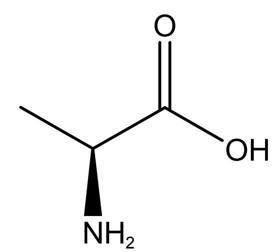
**(c) Nicotine**

**log $K_{ow}$ = 1.17**



**(d) Hexachlorobenzene**

**log $K_{ow}$ = 5.73**

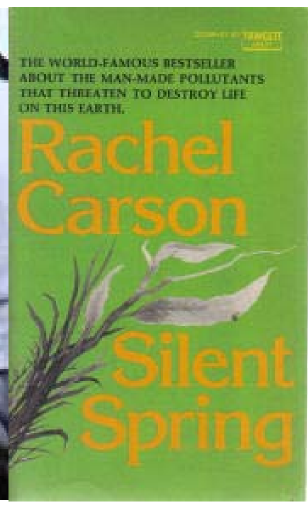


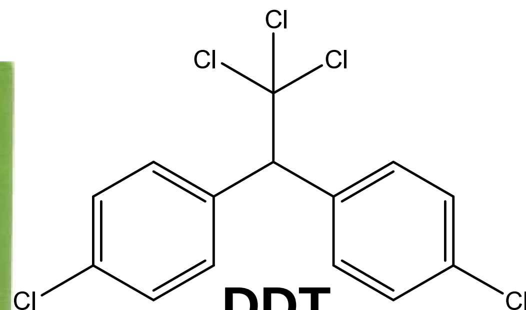
**(e) Alanine**

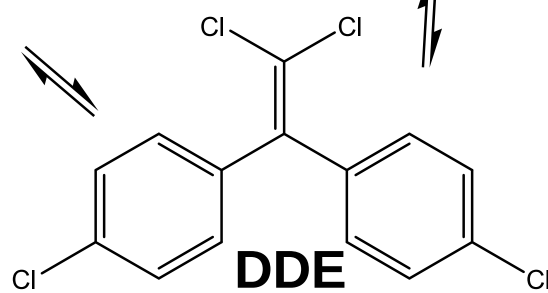
**log $K_{ow}$ = – 2.16**

# Chemistry & The Web of Life

- 1962: Rachel Carson, scientist & writer released "Silent Spring"
- Impact of excessive pesticide usage & species loss/human health
- Controversial issues: Agriculture/food production & disease prevention (malaria) *vs.* Long-term environment/health degradation

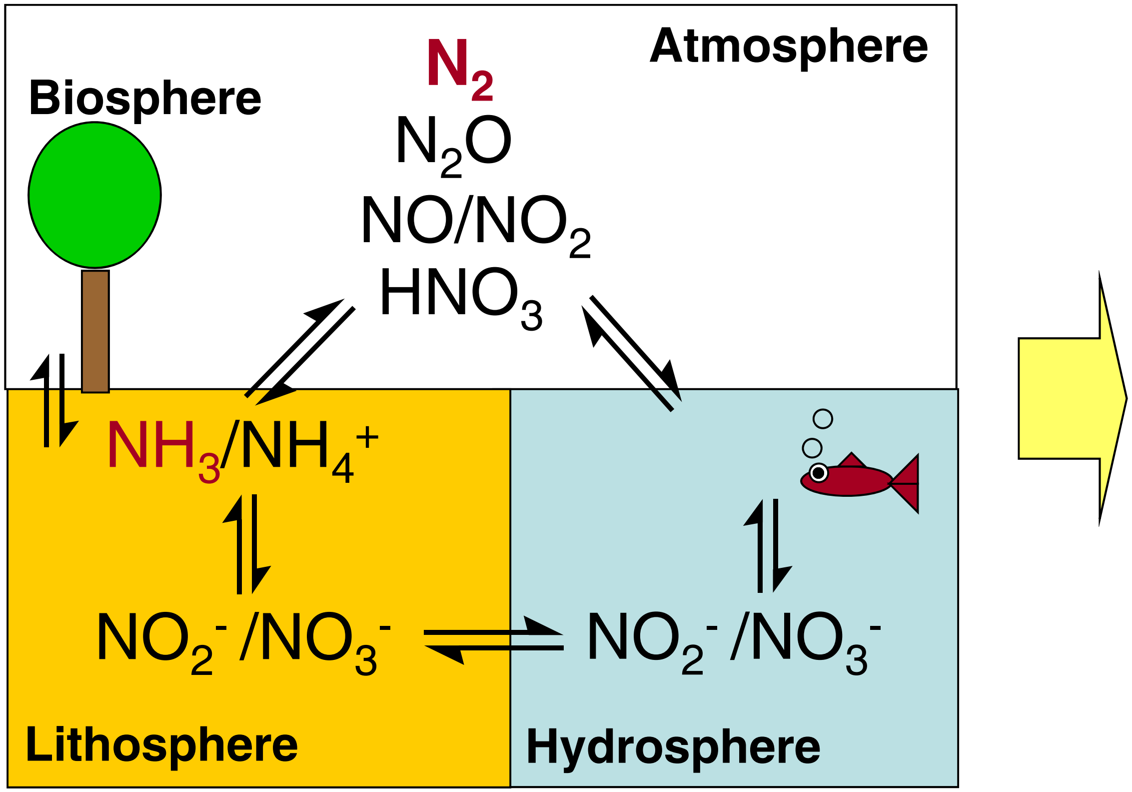



**1962** → DDT banned **1969** in Canada and **1972** in USA
Limited use by developing countries (malaria)

# The Nitrogen Biogeochemical Cycle

## Dynamic Equilibrium: N Transport/Transformation




**Nitrogen Fixation**

**Nitrification**

**Denitrification**

**Acid Rain**

**Leaching**

**Assimilation**

**Decay**

**Industrial $N_2$ Fixation: Haber-Bosch Process**

p. 652, 9th ed.

# Equilibrium & Le Châtelier's Principle

**Response to Stresses:** A system in dynamic equilibrium will respond to an external stress by relieving the stress in order to re-establish an equilibrium state

$K = K_p = 4.3 \times 10^{-3}$ **at 573K**

**Haber-Bosch Process**

*Exothermic Reaction*

$$N_2\,(g) + 3H_2\,(g) \overset{K}{\rightleftharpoons} 2NH_3\,(g) \quad \Delta H^o = -\,46.1\ \text{kJ/mol}$$

**Effect on yield of $NH_3$?**

1. **Increase pressure of $N_2$ →** ***Increase!***
2. **Decrease pressure of $NH_3$ →** ***Increase!***
3. **Increase Temperature →** ***Decrease!***
4. **Increase all pressures →** ***Increase!***

**Would a catalyst impact the yield?**

**Refer to Ch. 15-6, p. 673-679 (638-643, 652-6539th ed.)**

# Effect of increasing all partial pressures - by decreasing volume

Start with $N_2$, $H_2$ $N_2$ and $NH_3$ at equilibrium. Suppose the volume of the reaction vessel is reduced to one half its initial size. The partial pressures of $N_2$, $H_2$ and $NH_3$ are doubled.

(a) Is the gas mixture still at equilibrium?

(b) If not, in what direction does the reaction proceed?

After the pressures are increased, we have

$$Q = \frac{2^2 P^2_{\mathrm{NH_3},i}}{2P_{\mathrm{N_2},i} 2^3 P^3_{\mathrm{H_2},i}} = \frac{1}{4} \frac{P^2_{\mathrm{NH_3},i}}{P_{\mathrm{N_2},i} P^3_{\mathrm{H_2},i}} = \frac{1}{4} K < K$$

*(a)* $Q \neq K$ → not at equilibrium

*(b)* $Q < K$ → reaction proceeds towards products

# Haber-Bosch Process: Ammonia Synthesis

- A critical process for the manufacture of agricultural fertilizers (e.g., $NH_3$, $NH_4NO_3$) & explosives (e.g., TNT, Nitroglycerin)

$$N_2\,(g) + 3H_2\,(g) \overset{K_p}{\rightleftharpoons} 2NH_3\,(g) \quad \Delta H^o = -\,46.1\ \text{kJ/mol}$$

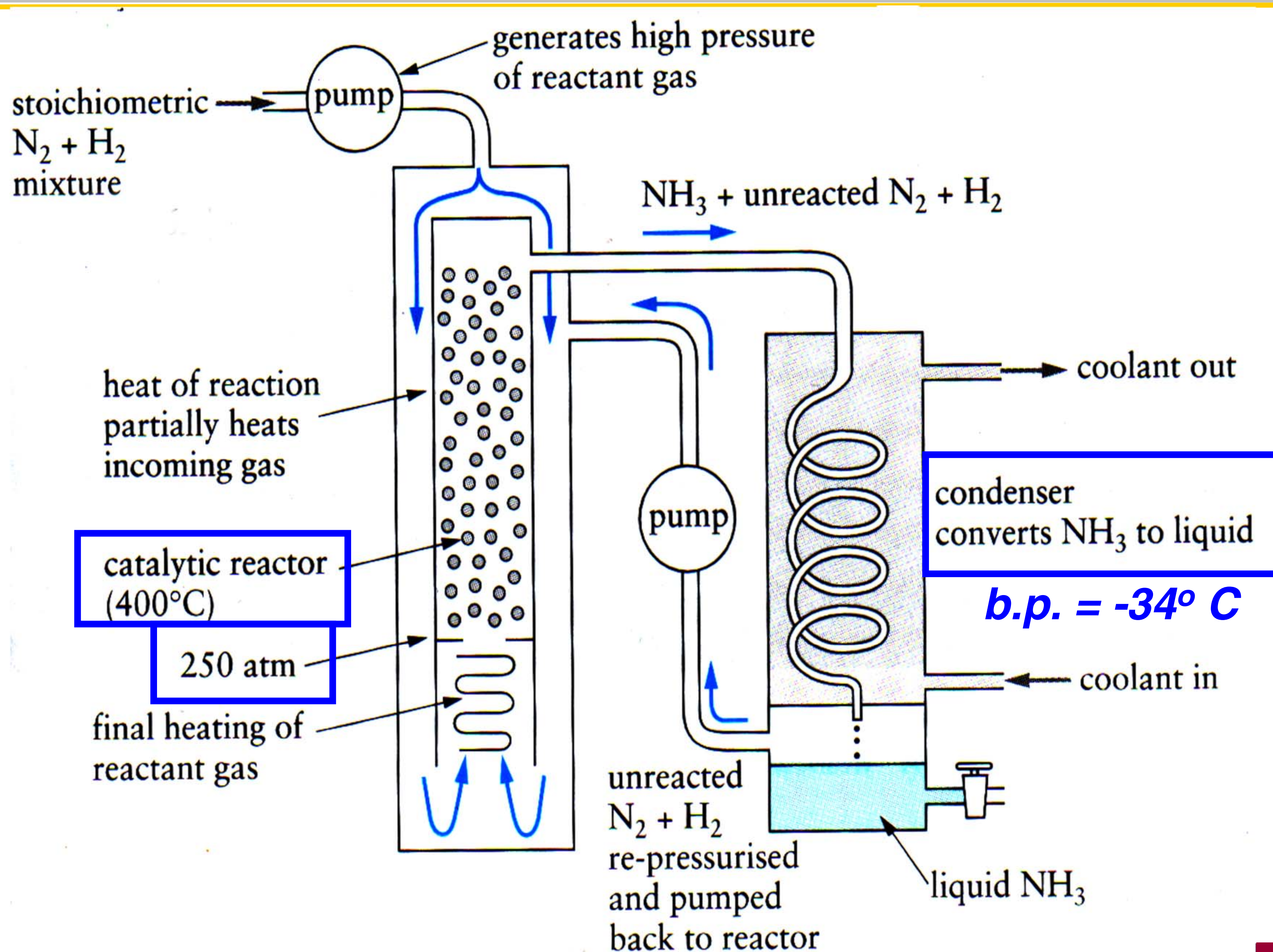
**Feedstocks**

$\mathbf{N_2}$ → Cyrogenic distillation of air (78% of air, b.p.= -196°C)

$\mathbf{H_2}$ → No natural source;
Steam reforming of methane

$$CH_4\,(g) + H_2O\,(g) \rightleftharpoons CO\,(g) + 3H_2\,(g)$$

# Haber-Bosch Process: An Elegant Design




***b.p. = -34° C***

# I-clicker Question #3

**Which gas has the highest boiling point (bp)?**

**(a) Hydrogen: $H_2$**

**(b) Nitrogen: $N_2$**

**(c) Ammonia: $NH_3$**

# Ammonium Nitrate: Pellets with a Punch

- Ammonia is a toxic, reactive and corrosive gas that is difficult to handle $\therefore$ Transform into solid ammonium nitrate, $NH_4NO_3$ (s)

$$NH_3\,(g) + HNO_3\,(aq) \longrightarrow NH_4NO_3\,(aq) \longrightarrow NH_4NO_3\,(s)$$


Instant cold packs!

Fertilizer pellets!

Explosives!

- But, how to produce nitric acid?
- Can we make it from ammonia?

# Nitric Acid Production: Aqua Fortis

- Ostwald Process is often used to produce nitric acid from the oxidation of ammonia and its dissolution in water

**Write a net balanced reaction: First 2 steps**

1. $4NH_3\,(g) + 5O_2\,(g) \rightleftharpoons 4NO\,(g) + 6H_2O\,(g)$ $\quad K_1$

**X 2** 2. $2NO\,(g) + O_2\,(g) \rightleftharpoons 2NO_2\,(g)$ $\quad K_2$

**Net:** $\boxed{4NH_3\,(g) + 7O_2\,(g) \rightleftharpoons 4NO_2\,(g) + 6H_2O\,(g)}$ $\quad K_{Net} = ?$

$$\boxed{K_{Net} = \frac{[H_2O]^6[NO_2]^4}{[NH_3]^4[O_2]^7}} = K_1\ K_2^2$$

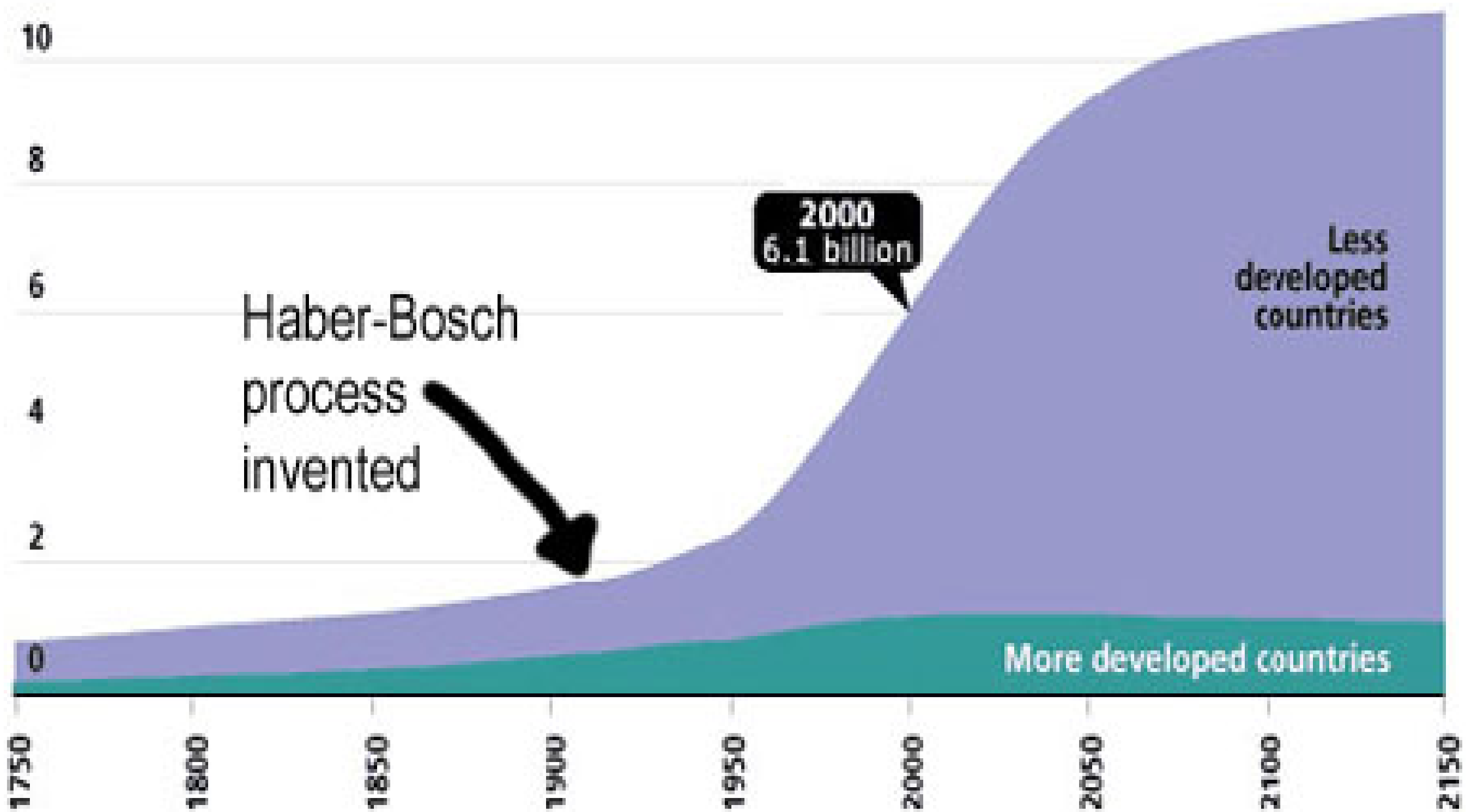
**Final step:**

3. $4NO_2\,(g) + O_2\,(g) + 2H_2O\,(l) \rightleftharpoons 4HNO_3\,(aq)$ $\quad K_3$

Ch. 15, p. 664-665 (629-631, 9th ed.)

# Chemistry and Population Growth?

**Population (in billions)**

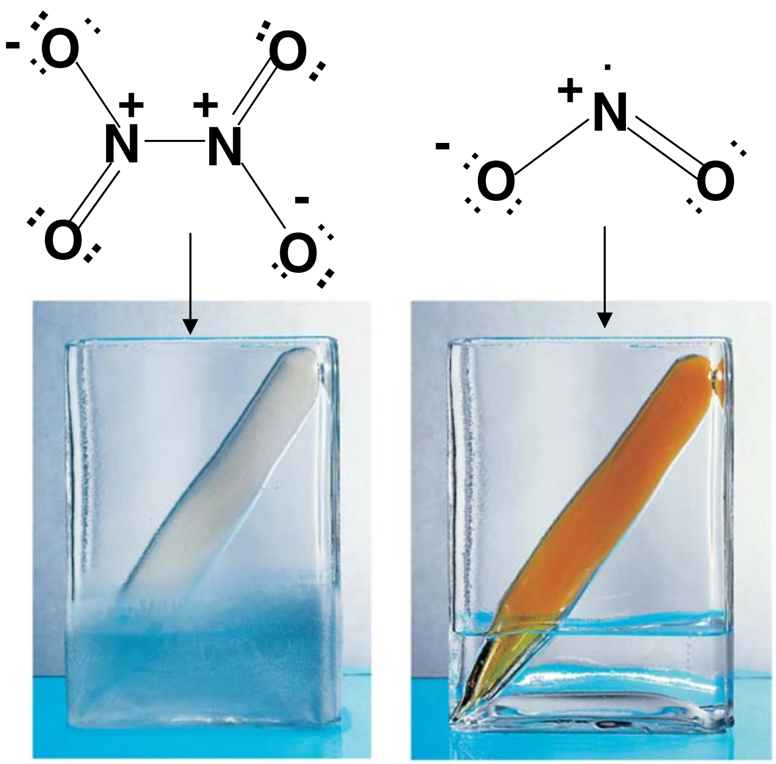


# Dinitrogen Tetraoxide

- Nitrogen dioxide is a toxic, reactive and gas irritant that can dimerize to form dinitrogen tetraoxide ($N_2O_4$)

$$N_2O_4\,(g) \overset{K}{\rightleftharpoons} 2NO_2\,(g) \qquad K = \frac{P_{NO_2}^2}{P_{N_2O_4}} = 11.4 \qquad \text{(at 25°C)}$$

ΔH° = +57.2 kJ/mol (Endothermic)



T=-25°C (a) (b) T= 25°C

**1. Is a mixture of 0.0205 moles $NO_2$ & 0.750 mol $N_2O_4$ in a 5.25 L flask at 25°C at equilibrium? If not, in what direction does the reaction shift?**

**2. What is K for the reverse reaction associated with dimerization of $NO_2$?**

Refer to Ch. 15, p. 680 (644, 9th ed.)

# Problems

**1**. Is a mixture of 0.0205 moles $NO_2$ & 0.750 mol $N_2O_4$ in a 5.25 L flask at 25°C at equilibrium? If not, in what direction does the reaction shift?

$$Q = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{(0.0205 \times 0.08206 \times 298.15 / 5.25)^2}{0.750 \times 0.08206 \times 298.15 / 5.25} = 0.0137 < K$$

Reaction will proceed in the forward direction – i.e. more $NO_2$ will be formed until equilibrium is re-established ($Q = K$).

**2**. What is $K$ for the reverse reaction associated with dimerization of $NO_2$?

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

$K_{reverse} = 1/K_{forward} = 1/11.4 = 0.0877$

# $N_2O_4$ Equilibrium Calculation

If you start with 1.00 atm $N_2O_4(g)$, what is partial pressure of $NO_2(g)$ when the system reaches equilibrium at 25°C

$$N_2O_4\,(g) \overset{K}{\rightleftharpoons} 2NO_2\,(g)$$

| | $N_2O_4$ (g) | $2NO_2$ (g) |
|---|---|---|
| Initial | 1.00 | 0 |
| Change | -x | +2x |
| Eq'm | 1.00-x | 2x |

$K$ = 11.4 at 25°C

**"ICE" Table**

here we use partial pressures in atm

- units are suppressed

At equilibrium, we have

$$K = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{(2x)^2}{(1-x)} = 11.4$$

Quadratic equation!

Ch. 15-7, p. 679-685 (644-650, 9th ed.)

# Solving the Quadratic

- Solving for *x*:

$$4x^2 = 11.4\left(1 - x\right)$$

**See Tutorial and Text for further examples of Equilibrium Calculations**

- Rearranged into standard quadratic form, gives:

$$4x^2 + 11.4x - 11.4 = 0$$

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

**Quadratic formula**

**(Note: Casio fx991 will solve this)**

$\boxed{x = 0.7842atm}$ or $x = -3.634atm$

(but negative P makes no sense)

Therefore $P_{NO2} = 2x = 1.568$ atm at equilibrium

# Take Home Problem

A sample of $NH_4HS(s)$ is placed in a 2.58 L flask containing 0.100 mol $NH_3(g)$. What will be the total gas pressure in the flask when equilibrium is established at 25°C?

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g) \quad K = 0.108 \text{ at } 25°C$$

**Solve for initial pressure of $NH_3$ (note $K = K_p$):**

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

$$P = \frac{0.100\,\text{mol} \times 0.08206\,\text{L atm K}^{-1}\text{mol}^{-1} \times 298\,\text{K}}{2.58\,\text{L}}$$

$$P = 0.948\,\text{atm}$$

# Solution

| $NH_4HS(s)$ | $\rightleftharpoons$ | $NH_3(g)$ | + | $H_2S(g)$ | $K = 0.108$ at 25°C |
|---|---|---|---|---|---|
| Initial | | 0.948 atm | | 0 atm | |
| Change | | +x | | +x | |
| Eq'm | | 0.948+x | | x | |

$$K_P = P_{NH_3} P_{H_2S} = 0.108$$

$$0.108 = (0.948 + x)(x)$$

$$x^2 + 0.948 - 0.108 = 0$$

Solve for x (quadratic):

$$x = 0.103 \text{ atm}, -0.105 \text{ atm}$$

(Negative P makes no sense)

$$P_{TOTAL} = P_{NH_3} + P_{H_2S}$$

$$P_{TOTAL} = (0.948 + x) + x$$

$$= 0.948 + 2x$$

$$P_{TOTAL} = 0.948 + (2x0.103)$$

$$= 1.154 atm$$


Department of Chemistry