

CHEMICAL EQUILIBRIUM

Reversibility and Chemical Change

- Equilibrium vapor pressure
 - Evaporation and condensation
 - Triple point conditions
- Chemical Reactions:
 - $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 - $\text{CaCO}_3(\text{s}) + 2\text{NaCl}(\text{s}) \rightleftharpoons \text{CaCl}_2(\text{s}) + \text{Na}_2\text{CO}_3(\text{s})$

Chemical equilibrium

- **Reversibility** is a general property of chemical change.
- **Macroscopic reversibility** depends on law of mass action:
 - Rate of a reaction is a function of how much material is reacting (concentration or partial pressure).
 - Chemical equilibrium is achieved when the rate of the forward reaction equals the rate of the reverse.
 - Phase changes often accompany chemical change.
- **Le Chatelier's Principle**:
 - Systems at equilibrium try to stay in equilibrium and respond to external stresses accordingly.

Systems at Equilibrium

- Systems move spontaneously toward equilibrium.
- Equilibrium is a dynamic state.
- Approach to equilibrium is independent of direction.
- Trade-off between organization and randomization.

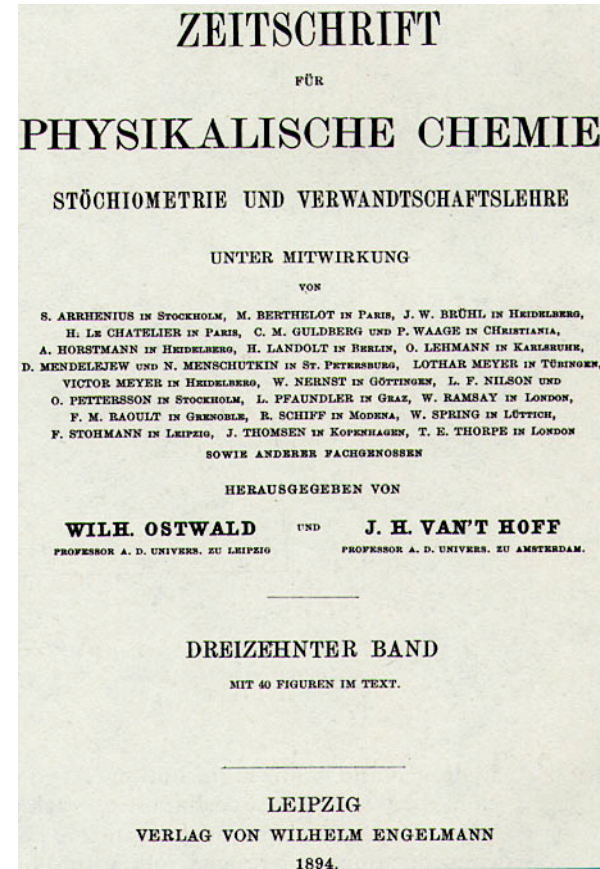
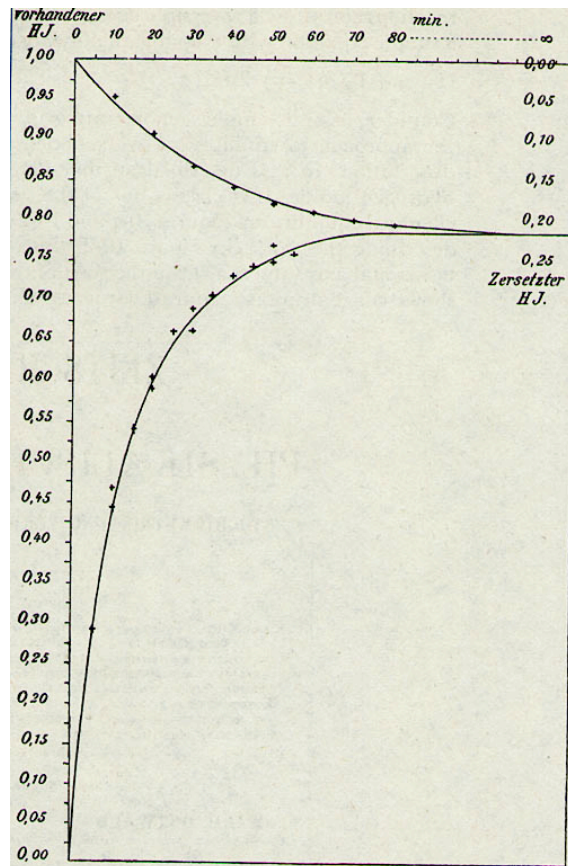
CHEMICAL EQUILIBRIUM

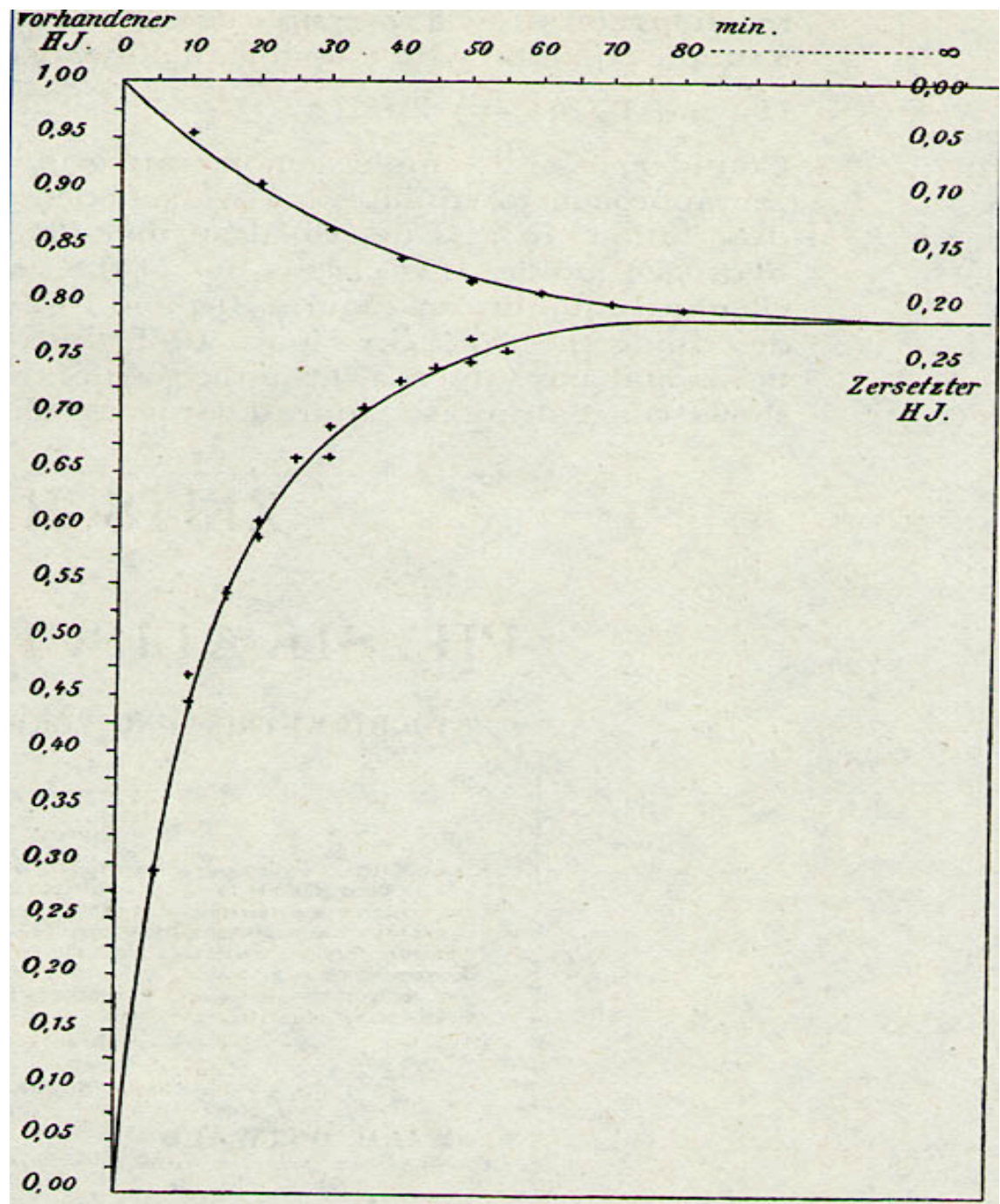


- Drive toward maximum entropy:
 - Favors bond dissociation, converting H_2 molecules to free H atoms.
 - Energy is required.
 - Equilibrium shifts to the right.
- Drive to achieve minimum energy
 - favors bond formation and H_2 molecules over free H atoms.
 - Equilibrium shifts to the left..

Hydrogen Iodide

Synthesis and Decomposition





ZEITSCHRIFT
FÜR
PHYSIKALISCHE CHEMIE

STÖCHIOMETRIE UND VERWANDTSCHAFTSLEHRE

UNTER MITWIRKUNG

VON

S. ARRHENIUS IN STOCKHOLM, M. BERTHELOT IN PARIS, J. W. BRÜHL IN HEIDELBERG,
H. LE CHATELIER IN PARIS, C. M. GULDBERG UND P. WAAGE IN CHRISTIANIA,
A. HORSTMANN IN HEIDELBERG, H. LANDOLT IN BERLIN, O. LEHMANN IN KARLSRUHE,
D. MENDELEJEW UND N. MENSCHUTKIN IN ST. PETERSBURG, LOTHAR MEYER IN TÜBINGEN,
VICTOR MEYER IN HEIDELBERG, W. NERNST IN GÖTTINGEN, L. F. NILSON UND
O. PETERSSON IN STOCKHOLM, L. PFAUNDLER IN GRAZ, W. RAMSAY IN LONDON,
F. M. RAOULT IN GRENOBLE, R. SCHIFF IN MODENA, W. SPRING IN LÜTTICH,
F. STOHMANN IN LEIPZIG, J. THOMSEN IN KOPENHAGEN, T. E. THORPE IN LONDON
SOWIE ANDERER FACHGENOSSEN

HERAUSGEGEBEN VON

WILH. OSTWALD UND **J. H. VAN'T HOFF**
PROFESSOR A. D. UNIVERS. ZU LEIPZIG PROFESSOR A. D. UNIVERS. ZU AMSTERDAM.

DREIZEHNTER BAND

MIT 40 FIGUREN IM TEXT.

LEIPZIG
VERLAG VON WILHELM ENGELMANN

1894.

The Equilibrium Constant

- For a general reaction:
 $aA + bB \rightleftharpoons cC + dD$

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

$$K_p = \frac{p^c p^d}{p^a p^b}$$

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

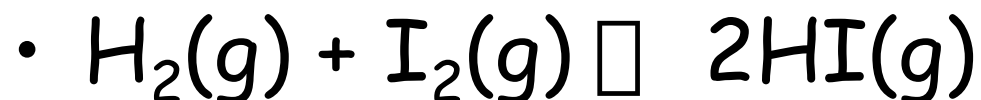
- p = partial pressure, usually measured in units of torr or atm.
- $[\text{conc}] = [\text{mol/L}]$
 Δn = difference in moles (n) of products and reactants:

$$\Delta n = n_p - n_r$$

The Equilibrium Constant



$$K = [\text{H}_2][\text{I}_2]/[\text{HI}]^2$$

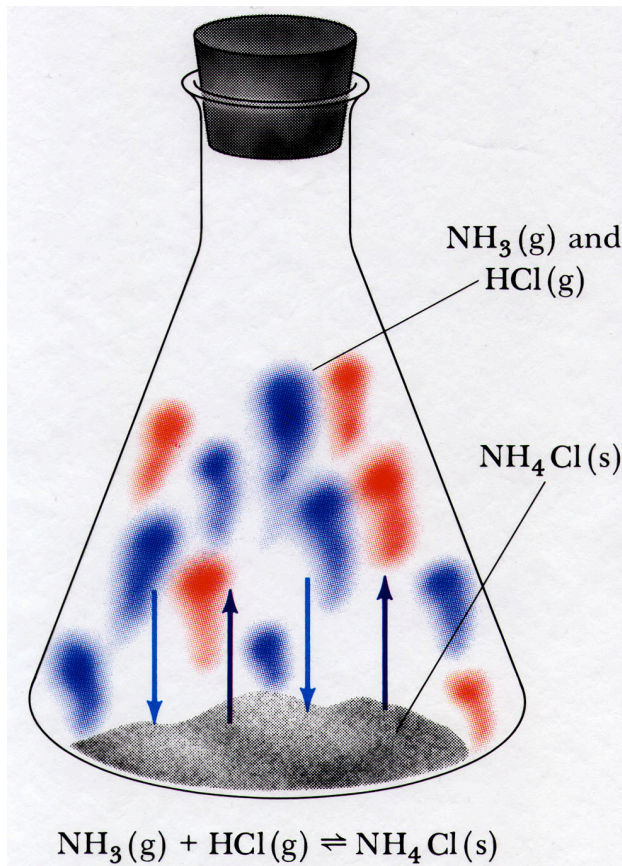


$$K' = 1/K = [\text{HI}]^2/[\text{H}_2][\text{I}_2]$$



Ammonium Chloride

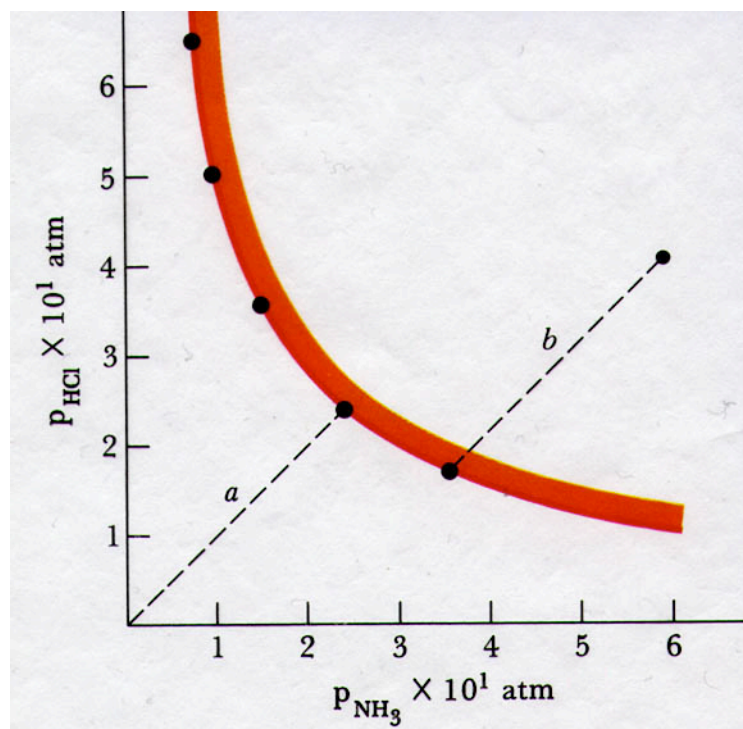
Synthesis and Decomposition



- Chemical equilibrium is achieved from either direction
- Equilibrium depends on...
 - Temperature
 - Pressure
 - Moles of reactants and products

TABLE 10-1 Partial Pressures of NH_3 (g) and HCl (g) in Equilibrium with NH_4Cl (s) at 300°C , in Atmospheres

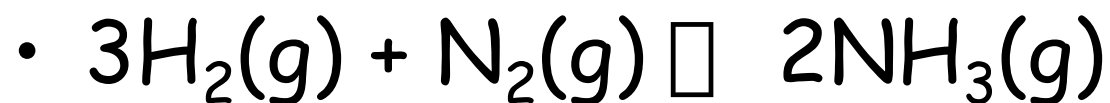
| Exp. # | p_{NH_3} | p_{HCl} | $K = p_{\text{NH}_3} \cdot p_{\text{HCl}}$ |
|--------|----------------------|----------------------|--|
| 1 | 2.3×10^{-1} | 2.3×10^{-1} | 5.3×10^{-2} |
| 2 | 3.1×10^{-1} | 1.8×10^{-1} | 5.6×10^{-2} |
| 3 | 4.0×10^{-1} | 1.4×10^{-1} | 5.6×10^{-2} |
| 4 | 4.9×10^{-1} | 1.1×10^{-1} | 5.4×10^{-2} |
| 5 | 6.0×10^{-1} | 9.2×10^{-2} | 5.5×10^{-2} |
| 6 | 1.7×10^{-1} | 3.2×10^{-1} | 5.4×10^{-2} |
| 7 | 1.2×10^{-1} | 4.5×10^{-1} | 5.4×10^{-2} |
| 8 | 8.9×10^{-2} | 6.2×10^{-1} | 5.5×10^{-2} |



The Equilibrium Constant

- $\text{NH}_4\text{Cl}(s) \rightleftharpoons \text{NH}_3(g) + \text{HCl}(g)$
 $K_c = [\text{NH}_3][\text{HCl}]$
 $K_p = p_{\text{NH}_3}p_{\text{HCl}}$
- $\text{NH}_3(g) + \text{HCl}(g) \rightleftharpoons \text{NH}_4\text{Cl}(s)$
 $K' = 1/K = [\text{NH}_3][\text{HCl}]$
 $K' = 1/K = 1/p_{\text{NH}_3}p_{\text{HCl}}$
- $K_p \neq K_c$ because $\Delta n \neq 0$

The Equilibrium Constant



$$K = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]}$$



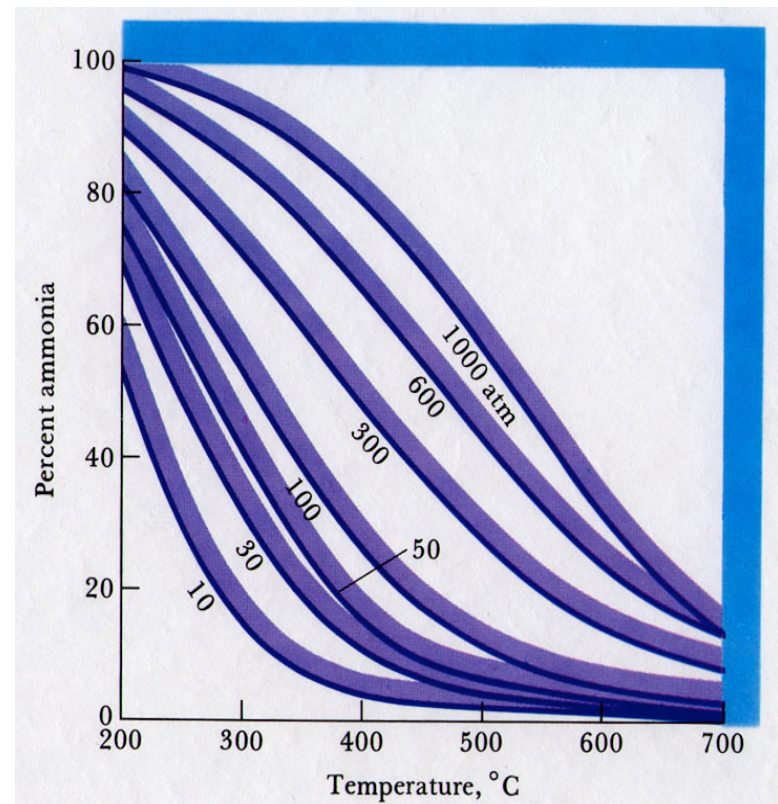
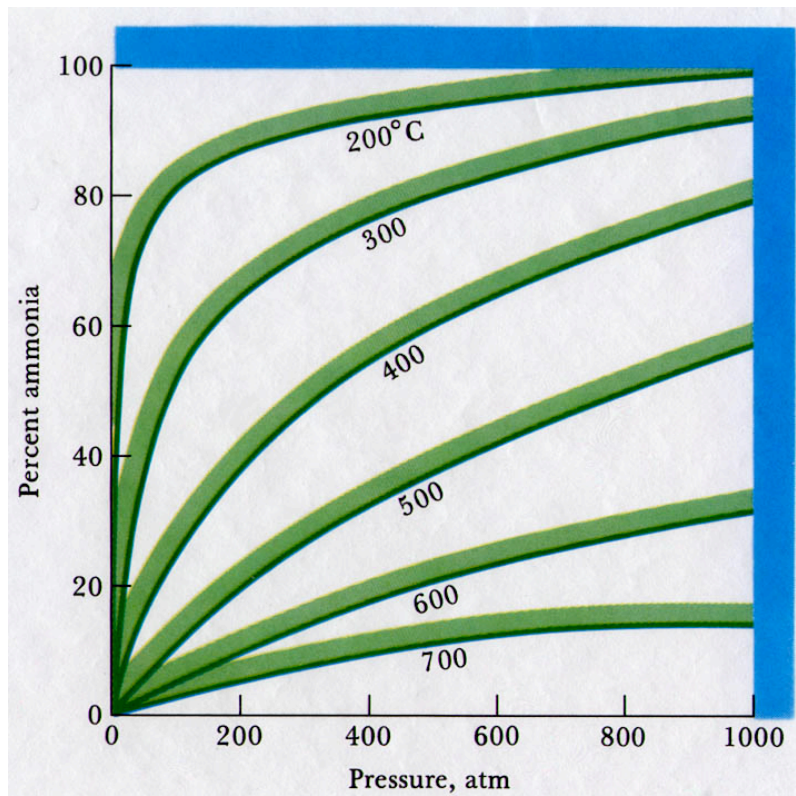
$$K' = 1/K = \frac{[\text{H}_2]^3[\text{N}_2]}{[\text{NH}_3]^2}$$

- $K_p \neq K_c$ because $\Delta n \neq 0$

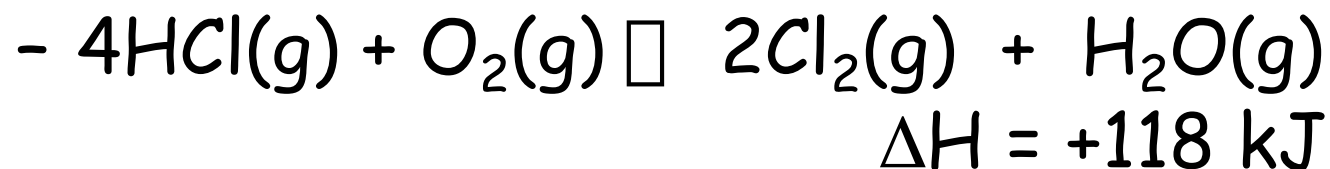
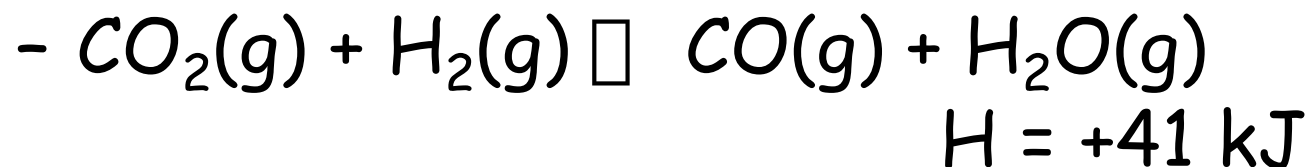
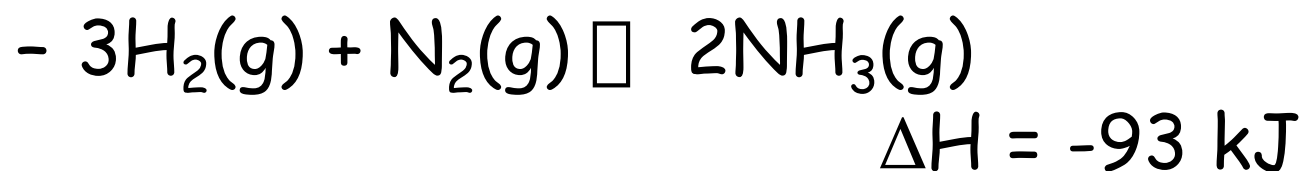
Le Chatelier's Principle

- Systems in equilibrium tend to stay in equilibrium unless acted upon by an external stress such as.....
 - changes in concentration
 - changes in temperature
 - changes in pressure/volume
- Catalysts alter only the rate at which equilibrium is achieved.

Ammonia Synthesis

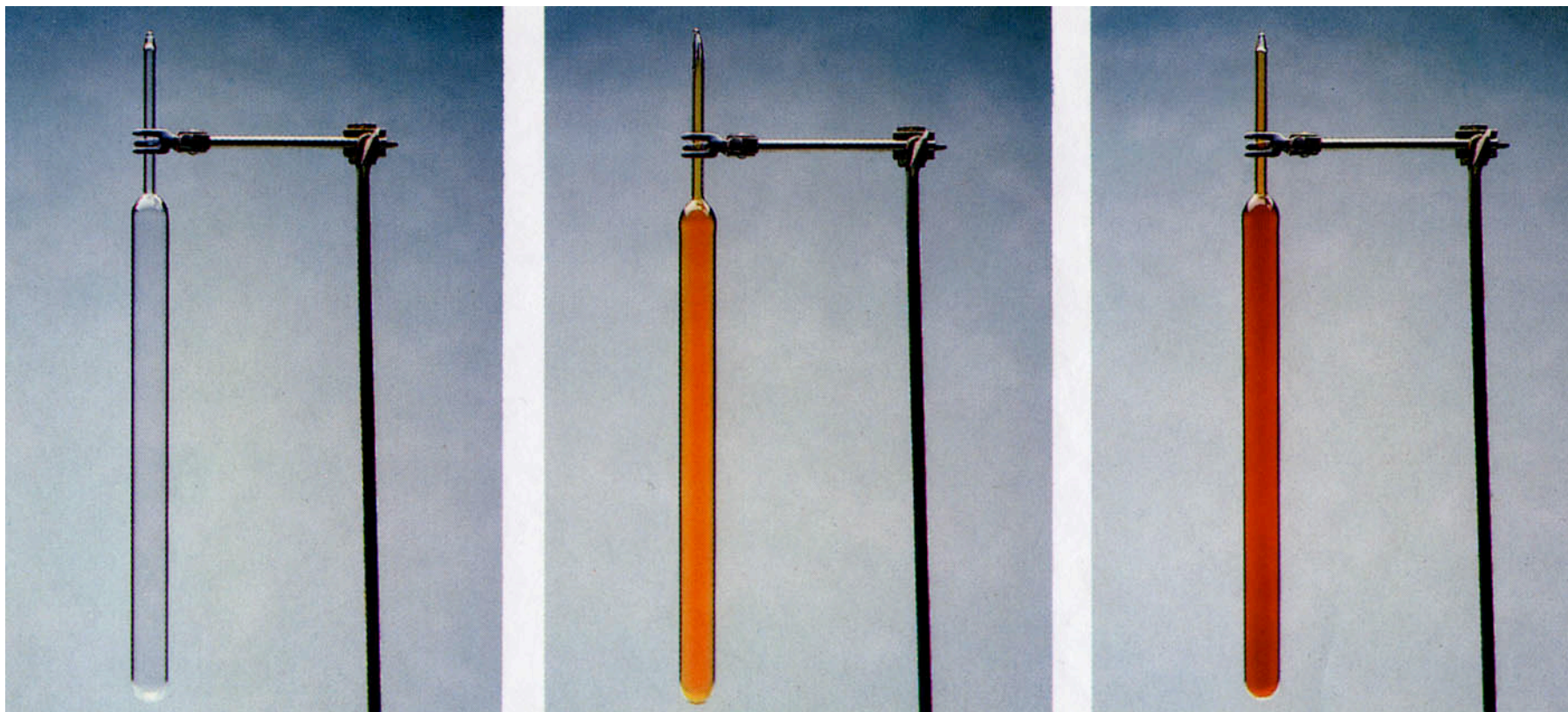


Le Chatelier's Principle



Examples

- Decomposition of nitrosyl bromide (NOBr)
 - $\text{NO}(g) + \text{Br}_2(g) \rightleftharpoons \text{NOBr}(g)$
- Carbon monoxide shift reaction
 - $\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$
- Hydrogen iodide formation
 - $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$



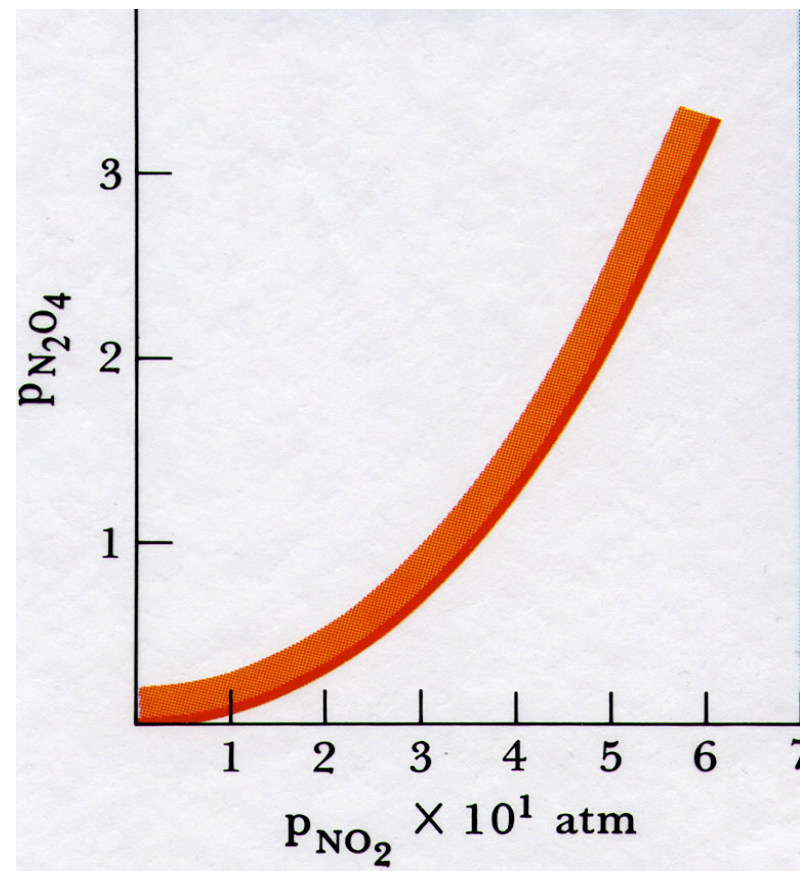
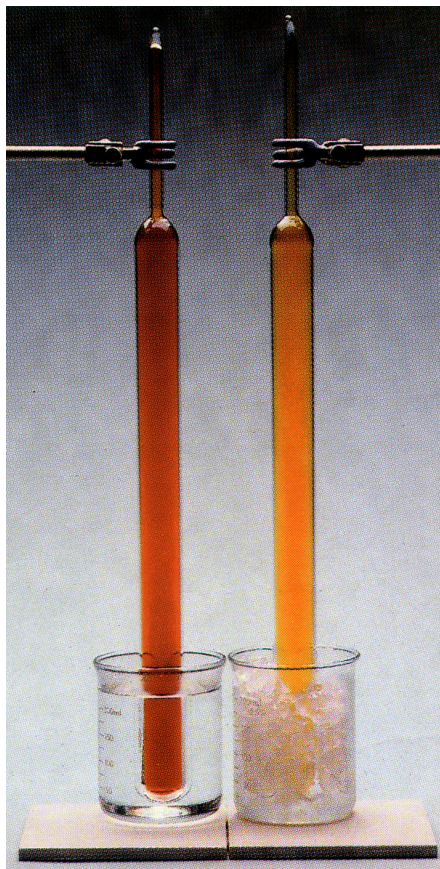
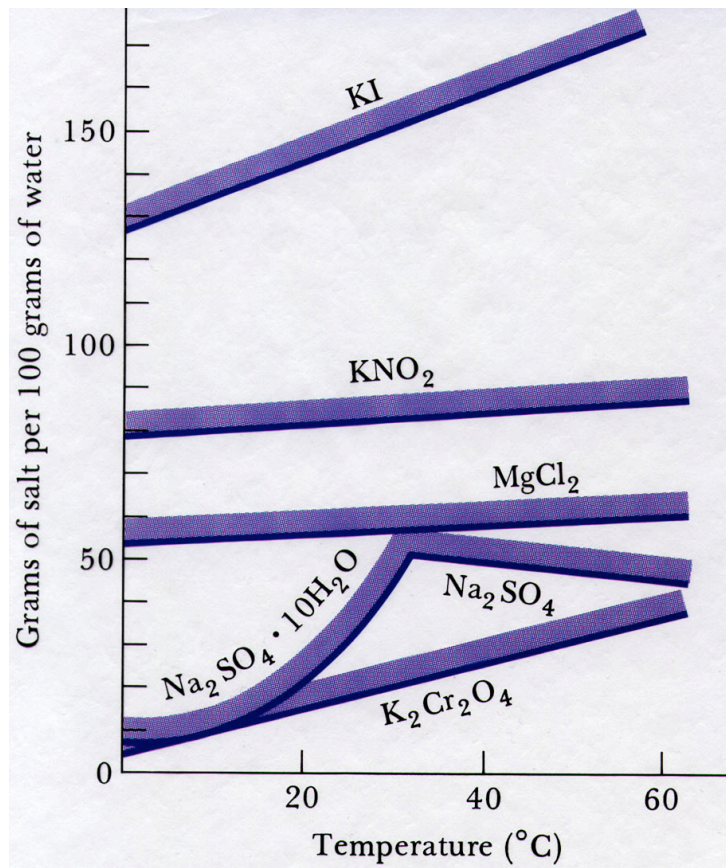




TABLE 10-2 Equilibrium Mixtures of NO_2 (g) and N_2O_4 (g) at 25°C

| p_{NO_2} | $p_{\text{N}_2\text{O}_4}$ | P_{total} | $K = \frac{p_{\text{N}_2\text{O}_4}}{p_{\text{NO}_2}^2}$ |
|----------------------|----------------------------|-----------------------|--|
| 1.0×10^{-2} | 8.8×10^{-4} | 1.1×10^{-2} | 8.8 |
| 2.0×10^{-2} | 3.5×10^{-3} | 2.4×10^{-2} | 8.8 |
| 4.0×10^{-2} | 1.4×10^{-2} | 5.4×10^{-2} | 8.8 |
| 8.0×10^{-2} | 5.6×10^{-2} | 1.36×10^{-1} | 8.8 |
| 1.6×10^{-1} | 2.3×10^{-1} | 3.9×10^{-1} | 9.0 |
| 3.2×10^{-1} | 9.0×10^{-1} | 1.22×10^0 | 8.8 |
| 6.4×10^{-1} | 3.6×10^0 | 4.2×10^0 | 8.8 |

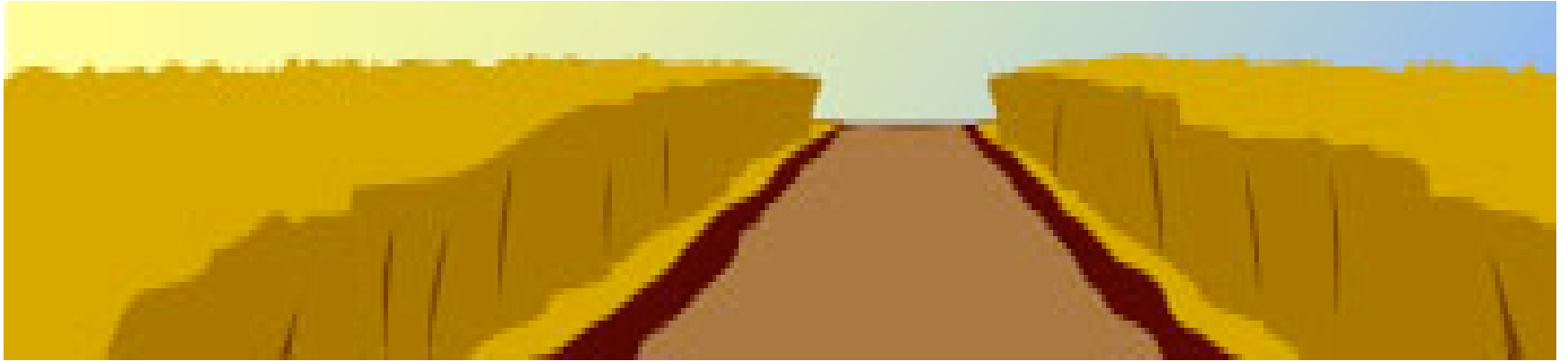
Soluble Salts in Water



- KI and K₂CrO₄:
 - Potassium iodide and chromate are soluble
 - Lead chromate and silver iodide are insoluble.... sparingly soluble:
 - K_{sp}(PbCrO₄)

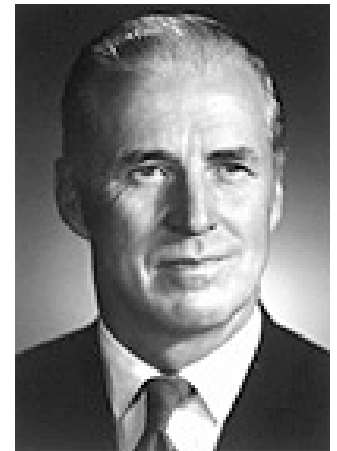
TABLE 12-2 Solubility Product Constants at 25°C

| Compound | K_{sp} | Compound | K_{sp} |
|---|----------------------------|---------------------|----------------------------|
| AgBr | 5.2×10^{-13} | MgCO ₃ | 4.0×10^{-5} |
| AgCl | 2.8×10^{-10} | Mg(OH) ₂ | 1.2×10^{-11} |
| Ag ₂ CrO ₄ | 1.9×10^{-12} | Mn(OH) ₂ | 1.0×10^{-14} |
| AgI | 8.5×10^{-17} | MnS | 1.4×10^{-15} |
| Ag ₂ S | 1.6×10^{-49} | Ni(OH) ₂ | 1.6×10^{-16} |
| Al(OH) ₃ | 1.8×10^{-33} | NiS | 1.4×10^{-24} |
| BaCO ₃ | 1.6×10^{-9} | PbCO ₃ | 1.5×10^{-13} |
| BaCrO ₄ | 8.5×10^{-11} | PbCrO ₄ | 1.8×10^{-14} |
| BaF ₂ | 1.7×10^{-6} | Pb(OH) ₂ | 1.8×10^{-16} |
| BaSO ₄ | 1.1×10^{-10} | PbS | 3.4×10^{-28} |
| CaCrO ₄ | 7.1×10^{-4} | PbSO ₄ | 1.3×10^{-8} |
| CaF ₂ | 1.7×10^{-10} | Sn(OH) ₂ | 5×10^{-26} |
| Ca ₃ (PO ₄) ₂ | 1.3×10^{-32} | SnS | 8×10^{-29} |
| Cu(OH) ₂ | 1.6×10^{-19} | SrCO ₃ | 1.6×10^{-9} |
| CuS | 8.5×10^{-45} | SrF ₂ | 2.8×10^{-9} |
| Fe(OH) ₂ | 1.6×10^{-15} | ZnCO ₃ | 2×10^{-10} |
| FeS | 3.7×10^{-19} | Zn(OH) ₂ | 4.5×10^{-24} |
| HgS | 3×10^{-53} | ZnS | 4.5×10^{-24} |



An agricultural scientist, Norman Borlaug was recognized By the Nobel Peace Prize in 1970 for his work on food and agriculture.

He often speculates that if Alfred Nobel had written his will to establish the various prizes and endowed them fifty years earlier, the first prize established would have been for food and agriculture. However, by the time Nobel wrote his will in 1895, there was no serious food production problem haunting Europe like the widespread potato famine in 1845-51, that took the lives of untold millions.



<http://www.nobel.se/peace/laureates/1970/>

The Equilibrium Constant

- For a general reaction:
 $aA + bB \rightleftharpoons cC + dD$

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

$$K_p = \frac{p^c p^d}{p^a p^b}$$

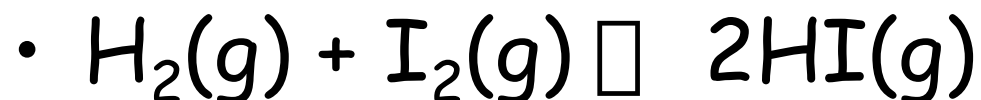
- $K_p = K_c (RT)^{\Delta n}$

- p = partial pressure, usually measured in units of torr or atm.
- $[\text{conc}] = [\text{mol/L}]$
 Δn = difference in moles (n) of products and reactants:
$$\Delta n = n_p - n_r$$

The Equilibrium Constant



$$K = [\text{H}_2][\text{I}_2]/[\text{HI}]^2$$



$$K' = 1/K = [\text{HI}]^2/[\text{H}_2][\text{I}_2]$$



The Equilibrium Constant

- $\text{NH}_4\text{Cl}(s) \rightleftharpoons \text{NH}_3(g) + \text{HCl}(g)$
 $K_c = [\text{NH}_3][\text{HCl}]$
 $K_p = p_{\text{NH}_3}p_{\text{HCl}}$
- $\text{NH}_3(g) + \text{HCl}(g) \rightleftharpoons \text{NH}_4\text{Cl}(s)$
 $K' = 1/K = [\text{NH}_3][\text{HCl}]$
 $K' = 1/K = 1/p_{\text{NH}_3}p_{\text{HCl}}$
- $K_p \neq K_c$ because $\Delta n \neq 0$

The Equilibrium Constant



$$K = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]}$$



$$K' = 1/K = \frac{[\text{H}_2]^3[\text{N}_2]}{[\text{NH}_3]^2}$$

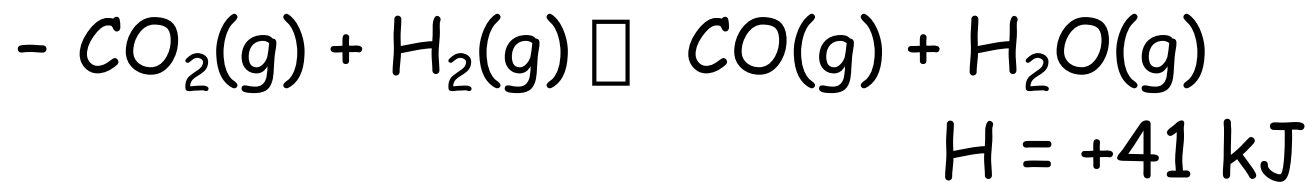
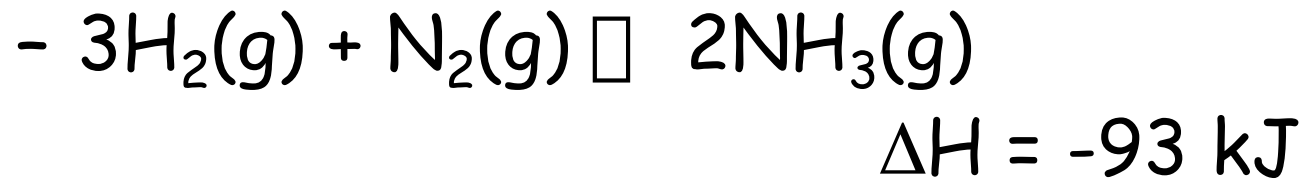


Le Chatelier's Principle

- Systems in equilibrium tend to stay in equilibrium unless acted upon by an external stress such as.....
 - changes in concentration
 - changes in temperature
 - changes in pressure/volume
- Catalysts alter only the rate at which equilibrium is achieved.

Le Chatelier's Principle

Enthalpy Change - Heat of Reaction



Examples

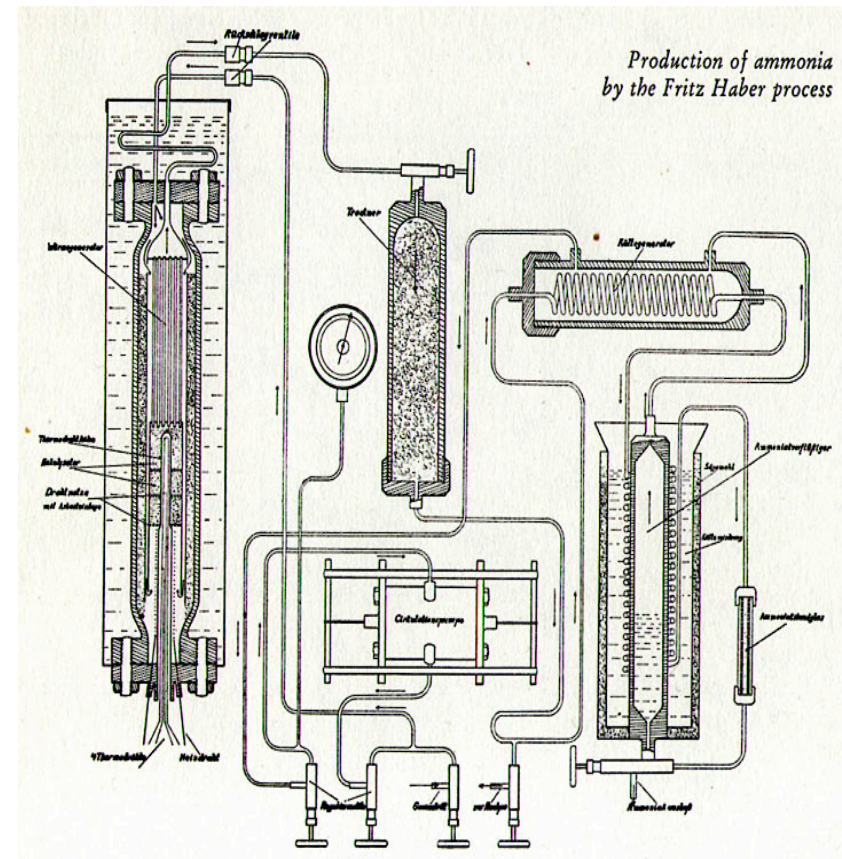
- Decomposition of nitrosyl bromide (NOBr)
 - $\text{NO}(g) + \text{Br}_2(g) \rightleftharpoons \text{NOBr}(g)$
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 - $\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$
- Hydrogen iodide formation
 - $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$

Fritz HABER



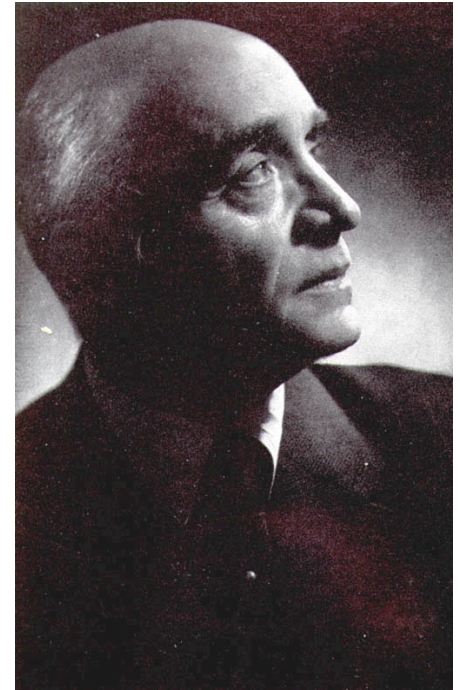
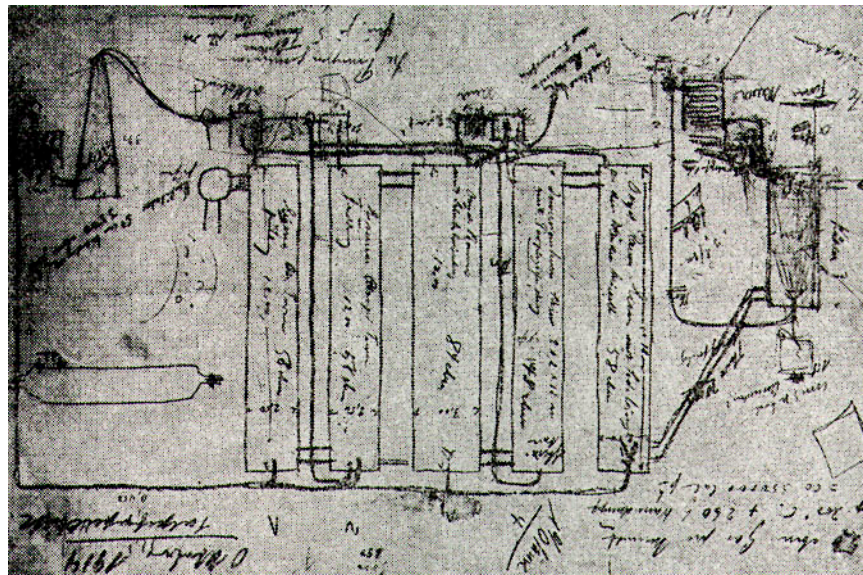
- Fertilizers/Explosives
 - Ammonium salts
 - Nitrates
 - Nitric acid
- Refrigerant
- Drugs-Dyes-Fibers
- Photography
- Household

Haber Ammonia



Carl
BOSCH

Friedrich
BERGIUS



Haber Ammonia



Haber Ammonia and War Reparations

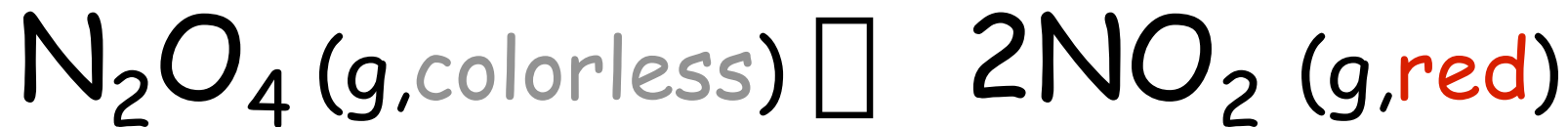
- 33 billion dollars = 50,000 tons of gold
 - Could not resort to...
 - Synthetic ammonia
 - Dye industry
 - German colonies
 - Estimated total gold content of the oceans:
 - 8 billion tons
 - Based on estimates of 5-10 mg/metric ton

Gold from seawater (1923)

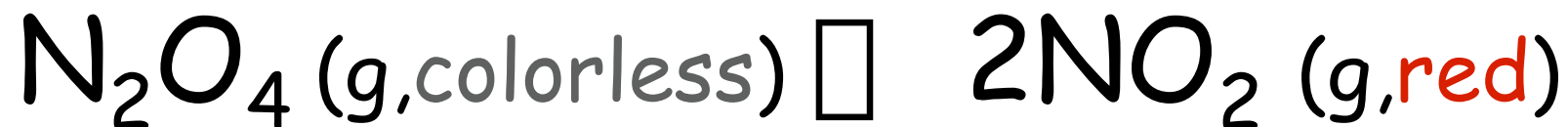
- Chemistry:

- Add lead acetate or mercuric nitrate, followed by ammonium sulfide, precipitating the sulfide (Au_2S)
- Separate silver by dissolving in nitric acid

- Alchemy



$$K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}} = \frac{\left(\frac{2x}{1+x} P_T \right)^2}{\left(\frac{1-x}{1+x} P_T \right)} = \frac{4x^2}{1-x^2} P_T$$



- Sample problem:

- Consider a mixture of N_2O_4 and NO_2 at a total pressure of 1.5 atm... resulting from the dissociation of N_2O_4 .
 - If $K_p = 0.14$ at the temperature of the experiment, what fraction of the N_2O_4 originally present dissociated?
- What happens if P_T falls to 1.0 atm?

Phosgene Decomposition

- $\text{COCl}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$
 - Write a general expression in terms of
 - the fraction α decomposed
 - the total pressure P_T
 - the equilibrium constant K_p
 - Demonstrates the pressure-dependency for an equilibrium system where $n \neq 0$



- If $K_p = 0.11$ at the temperature of the experiment, what is the the partial pressure of NH_3 ? Of H_2S ?
- Add solid NH_4HS into a reactor containing 0.50 atm of NH_3 and calculate the partial pressures of both gases at equilibrium.