Equilibrium Thermodynamics
Reversibility and Chemical Change

- Equilibrium vapor pressure
  - Evaporation and condensation
  - Triple point conditions
- Chemical Reactions:
  - $CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$
  - $CaCO_3(s) + 2NaCl(s) \Leftrightarrow CaCl_2(s) + Na_2CO_3(s)$

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.

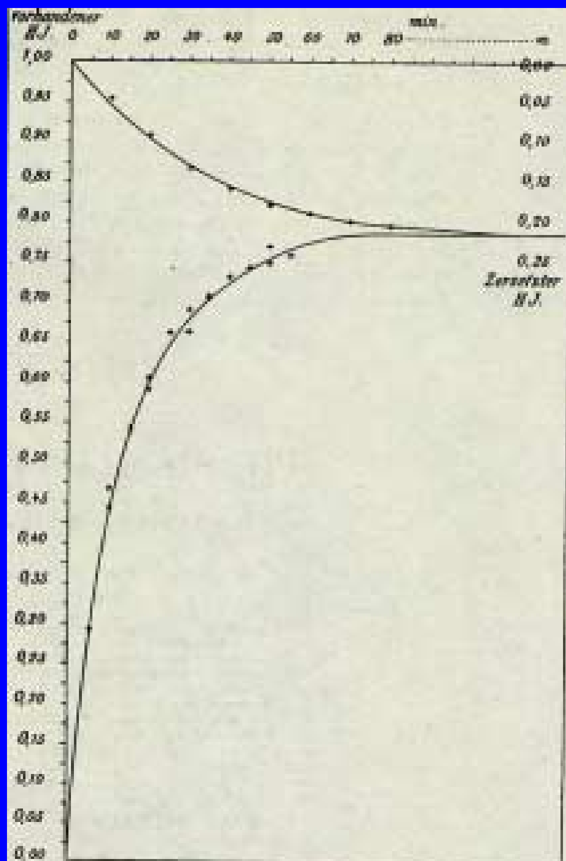
Simple System

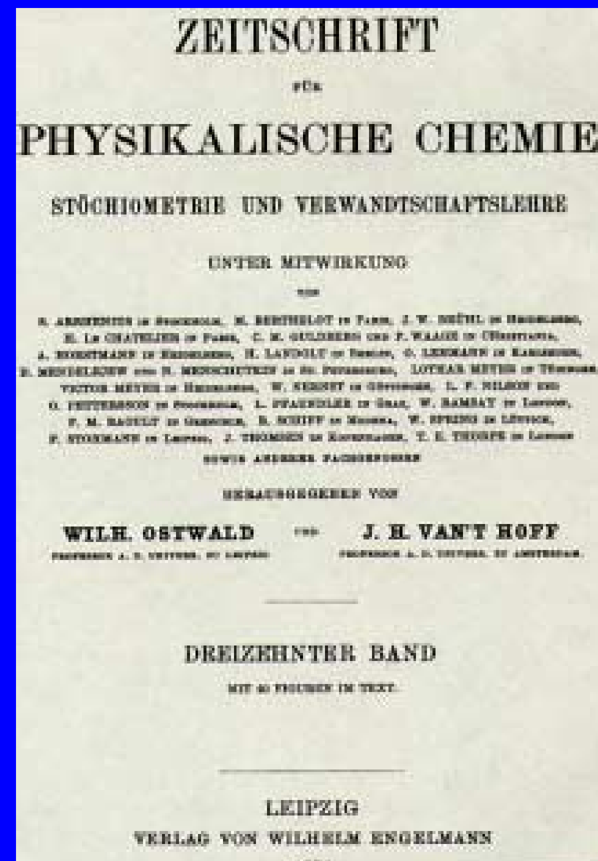
$$H_2(g) \Leftrightarrow 2H(g)$$

- 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

HERAUSGEGEBEN VON

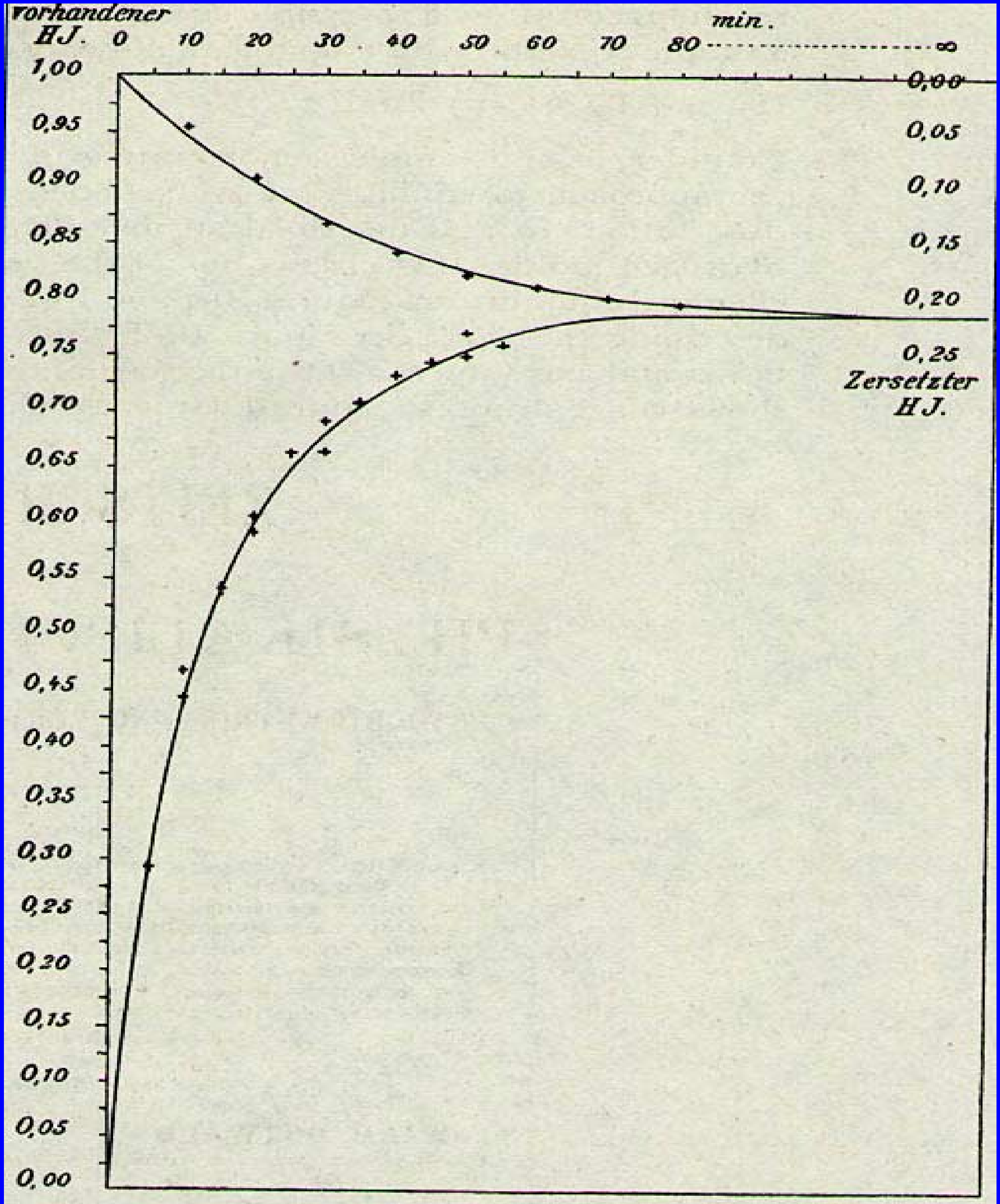
WILH. OSTWALD UND J. H. VAN'T HOFF

DREIZEHNTER BAND

LEIPZIG

VERLAG VON WILHELM ENGELMANN

1894.



vorhandener
H J.
min.
0
10
20
30
40
50
60
70
80
∞
1,00
0,95
0,90
0,85
0.80
0,75
0,70
0,65
0,60
0,55
0,50
0,45
0,40
0,35
0,30
0,25
0,20
0,15
0,10
0,05
0,00
0,00
0,05
0,10
0,15
0,20
0,25
Zersetzter
H J.

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. PETTERSSON 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⇔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.
- [conc] = [mol/L]
  Δn = difference in moles (n) of products and reactants:

$$\Delta n = n_p - n_r$$

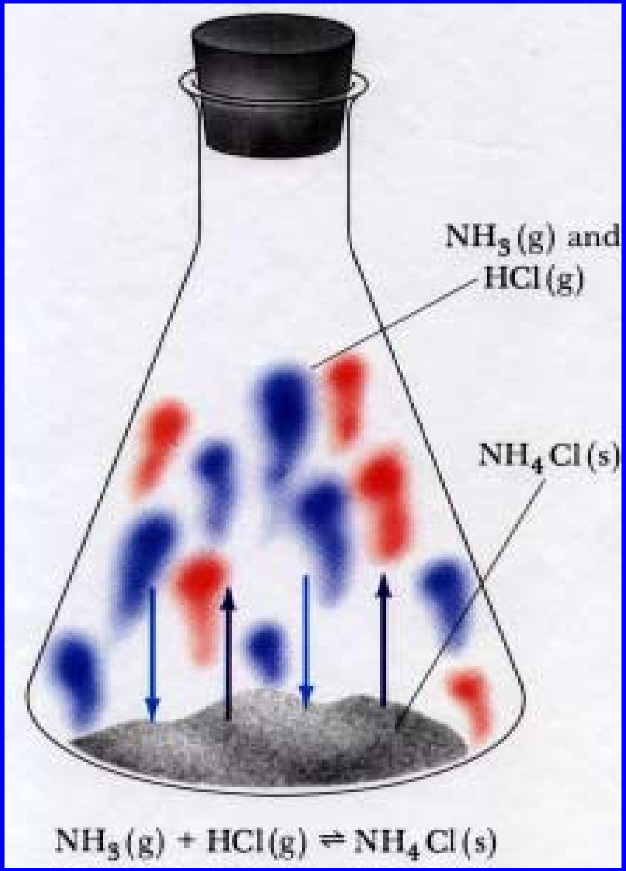
The Equilibrium Constant

- $2HI(g) \Leftrightarrow H_2(g) + I_2(g)$
  $K = [H_2][I_2]/[HI]^2$

- $H_2(g) + I_2(g) \Leftrightarrow 2HI(g)$
  $K' = 1/K = [HI]^2/[H_2][I_2]$

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

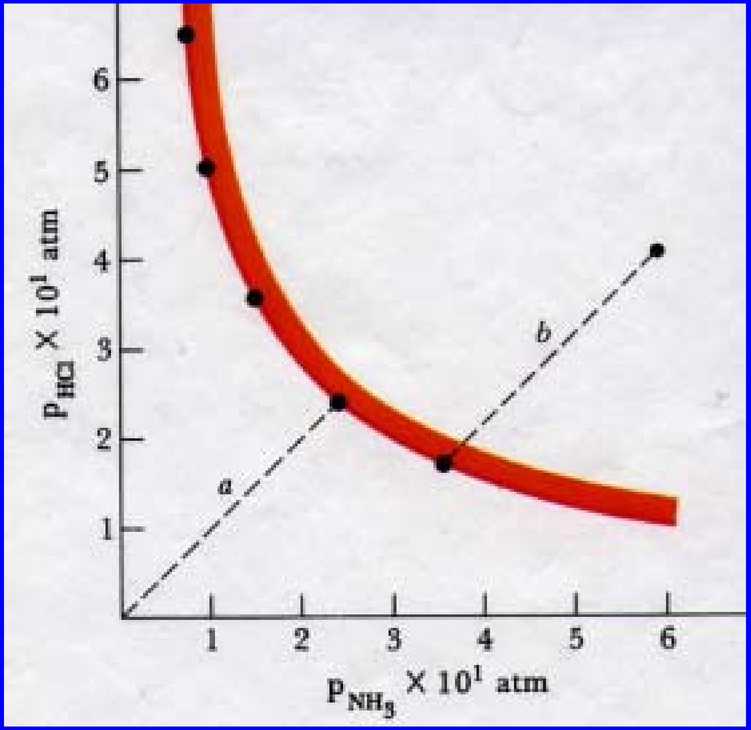
Ammonium Chloride
Synthesis and Decomposition



- 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}	$K = p_{NH_3} \cdot p_{HCl}$
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

- $NH_4Cl(s) \Leftrightarrow NH_3(g) + HCl(g)$

  $K_c = [NH_3][HCl]$

  $K_p = p_{NH3}p_{HCl}$

- $NH_3(g) + HCl(g) \Leftrightarrow NH_4Cl(s)$

  $K` = 1/K = [NH_3][HCl]$

  $K` = 1/K = 1/p_{NH3}p_{HCl}$

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

The Equilibrium Constant

- $3H_2(g) + N_2(g) \Leftrightarrow 2NH_3(g)$
  $K = [NH_3]^2/[H_2]^3[N_2]$

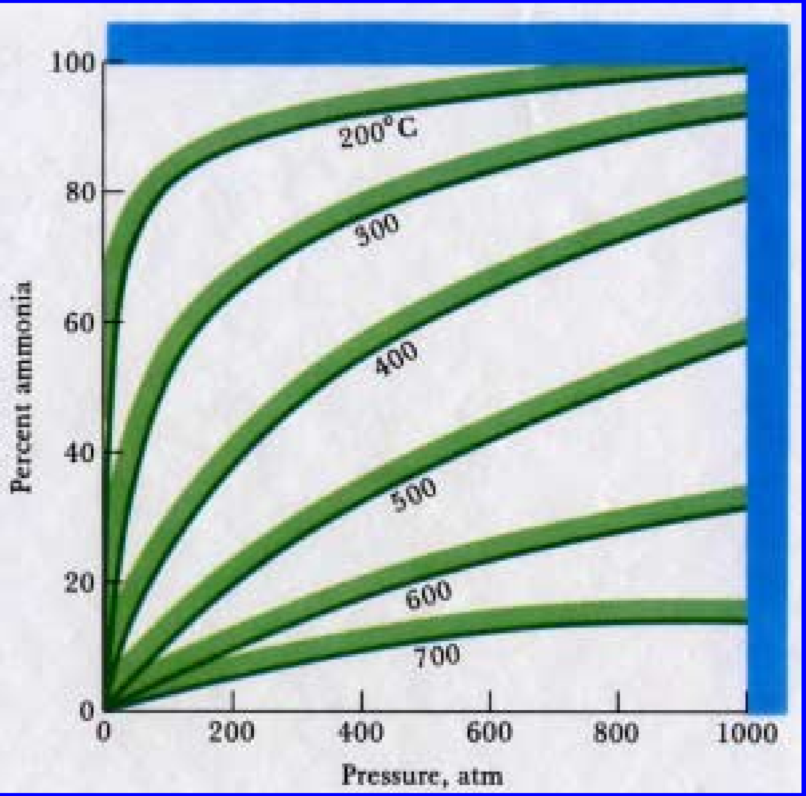
- $2NH_3(g) \Leftrightarrow 3H_2(g) + N_2(g)$
  $K` = 1/K = [H_2]^3[N_2]/ [NH_3]^2$

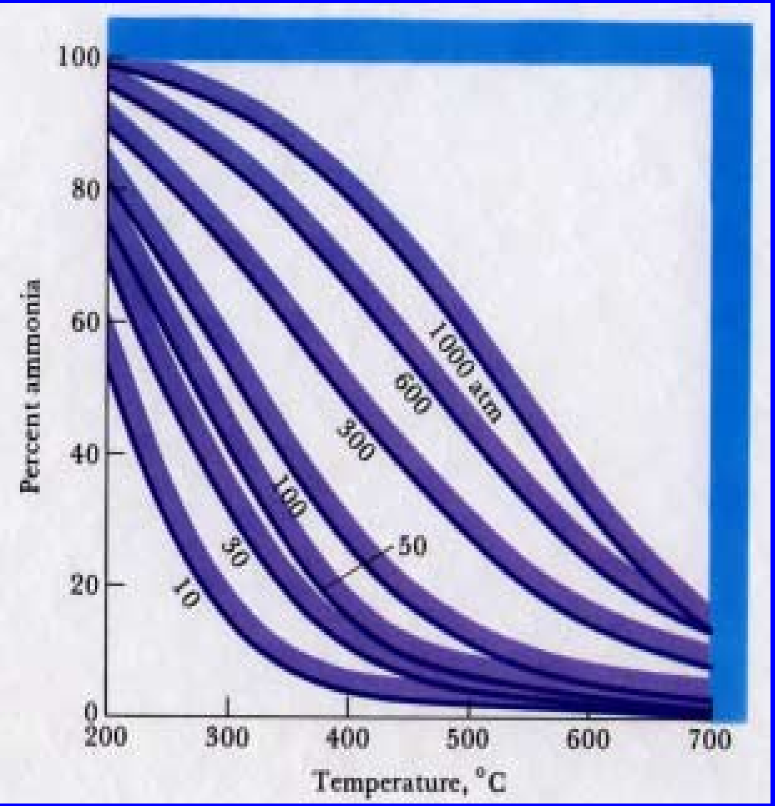
- $K_p \neq K_c$ because $\Delta n \neq 0$

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 <u>only</u> the rate at which equilibrium is achieved.

Ammonia Synthesis





Le Chatelier's Principle

- $3H_2(g) + N_2(g) \Leftrightarrow 2NH_3(g)$
  $\Delta H = -93\ kJ$

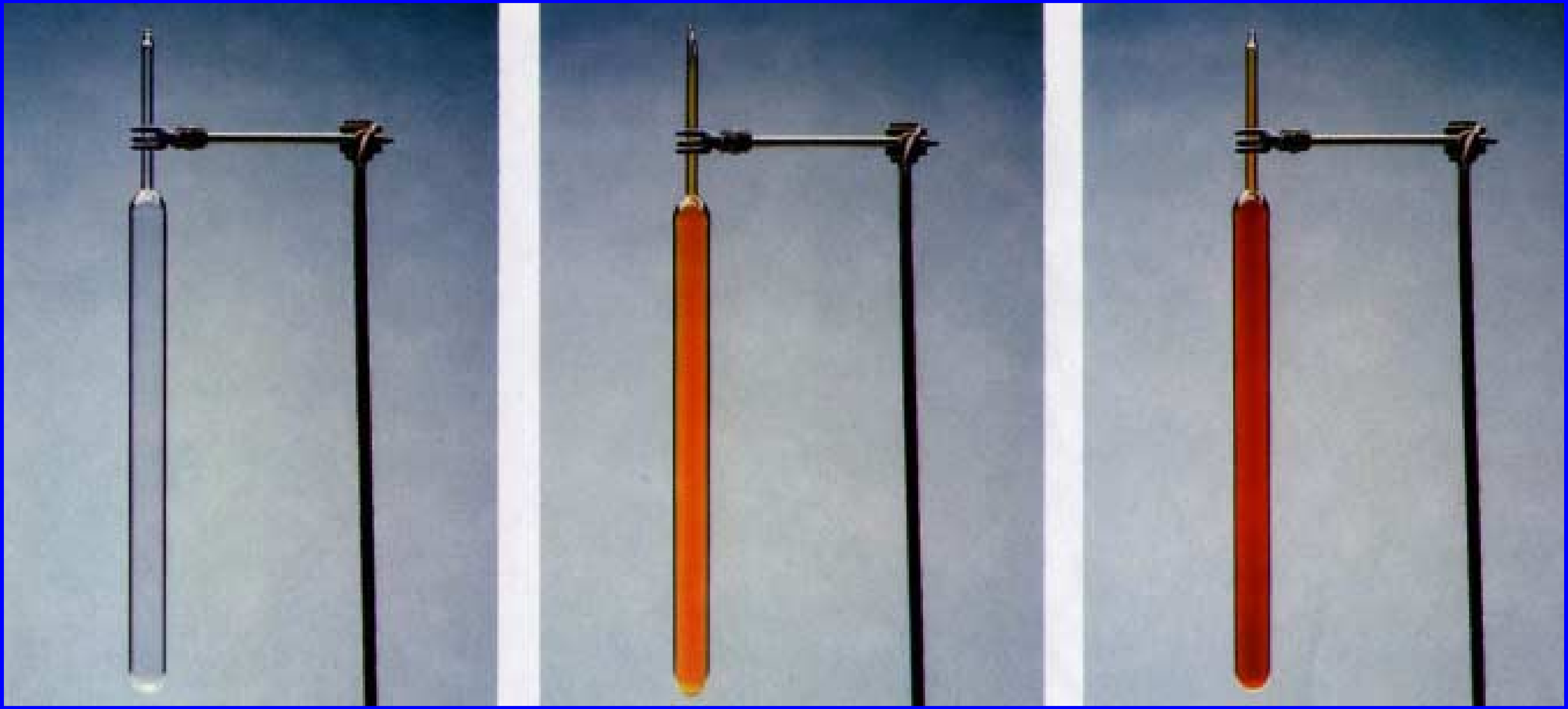
- $CO_2(g) + H_2(g) \Leftrightarrow CO(g) + H_2O(g)$
  $\Delta H = +41\ kJ$

- $4HCl(g) + O_2(g) \Leftrightarrow 2Cl_2(g) + H_2O(g)$
  $\Delta H = +118\ kJ$

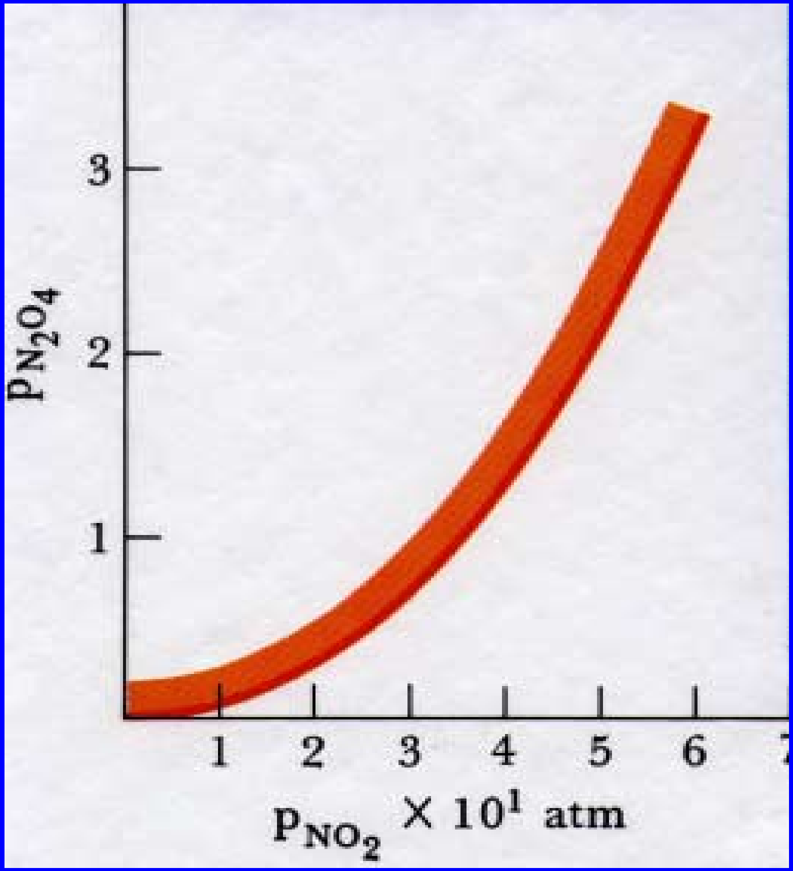
Examples

- Decomposition of nitrosyl bromide (NOBr)
  - $NO(g) + Br_2(g) \Leftrightarrow NOBr(g)$
- Carbon monoxide shift reaction
  - $CO(g) + H_2O(g) \Leftrightarrow CO_2(g) + H_2(g)$
- Hydrogen iodide formation
  - $H_2(g) + I_2(g) \Leftrightarrow 2HI(g)$

$2NO_2$ (colorless) $\Leftrightarrow$ N_2O_4 (red)



$2NO_2$ (colorless) $\Leftrightarrow$ N_2O_4 (red)

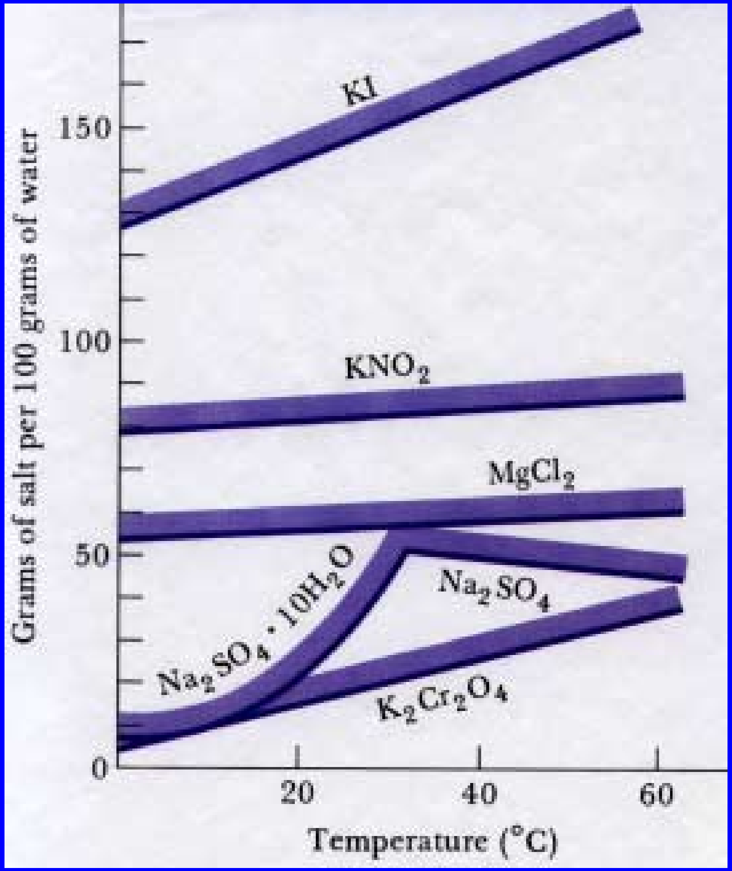


$2NO_2$ (colorless) $\Leftrightarrow$ N_2O_4 (red)

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

p_{NO_2}	$p_{N_2O_4}$	P_{total}	$K = \frac{p_{N_2O_4}}{p^2_{NO_2}}$
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

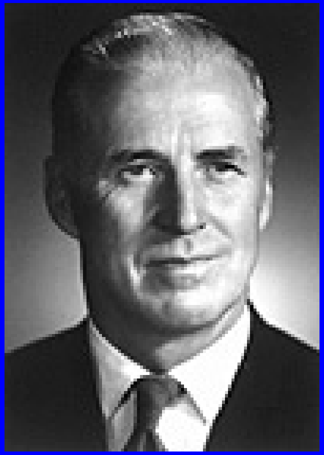
Soluble Salts in Water



- KI and K_2CrO_4:
  - Potassium iodide and chromate are soluble
  - Lead chromate and silver iodide are insoluble…. sparingly soluble:
    - Ksp(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_2CrO_4	1.9×10^{-12}	$Mn(OH)_2$	1.0×10^{-14}
AgI	8.5×10^{-17}	MnS	1.4×10^{-15}
Ag_2S	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⇔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.
- [conc] = [mol/L]
  Δn = difference in moles (n) of products and reactants:

$$\Delta n = n_p - n_r$$

The Equilibrium Constant

- $2HI(g) \Leftrightarrow H_2(g) + I_2(g)$

  $K = [H_2][I_2]/[HI]^2$

- $H_2(g) + I_2(g) \Leftrightarrow 2HI(g)$

  $K' = 1/K = [HI]^2/[H_2][I_2]$

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

The Equilibrium Constant

- $NH_4Cl(s) \Leftrightarrow NH_3(g) + HCl(g)$

  $K_c = [NH_3][HCl]$

  $K_p = p_{NH3}p_{HCl}$
- $NH_3(g) + HCl(g) \Leftrightarrow NH_4Cl(s)$

  $K` = 1/K = [NH_3][HCl]$

  $K` = 1/K = 1/p_{NH3}p_{HCl}$
- $K_p \neq K_c$ because $\Delta n \neq 0$

The Equilibrium Constant

- $3H_2(g) + N_2(g) \Leftrightarrow 2NH_3(g)$
  $K = [NH_3]^2/[H_2]^3[N_2]$

- $2NH_3(g) \Leftrightarrow 3H_2(g) + N_2(g)$
  $K` = 1/K = [H_2]^3[N_2]/ [NH_3]^2$

- $K_p \neq K_c$ 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 <u>only</u> the rate at which equilibrium is achieved.

Le Chatelier's Principle
Enthalpy Change - Heat of Reaction

- $3H_2(g) + N_2(g) \Leftrightarrow 2NH_3(g)$
  $\Delta H = -93\ kJ$

- $CO_2(g) + H_2(g) \Leftrightarrow CO(g) + H_2O(g)$
  $\Delta H = +41\ kJ$

Examples

- Decomposition of nitrosyl bromide (NOBr)
  - $NO(g) + Br_2(g) \Leftrightarrow NOBr(g)$
- Carbon monoxide shift reaction
  - $CO(g) + H_2O(g) \Leftrightarrow CO_2(g) + H_2(g)$
- Hydrogen iodide formation
  - $H_2(g) + I_2(g) \Leftrightarrow 2HI(g)$

Haber Ammonia

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

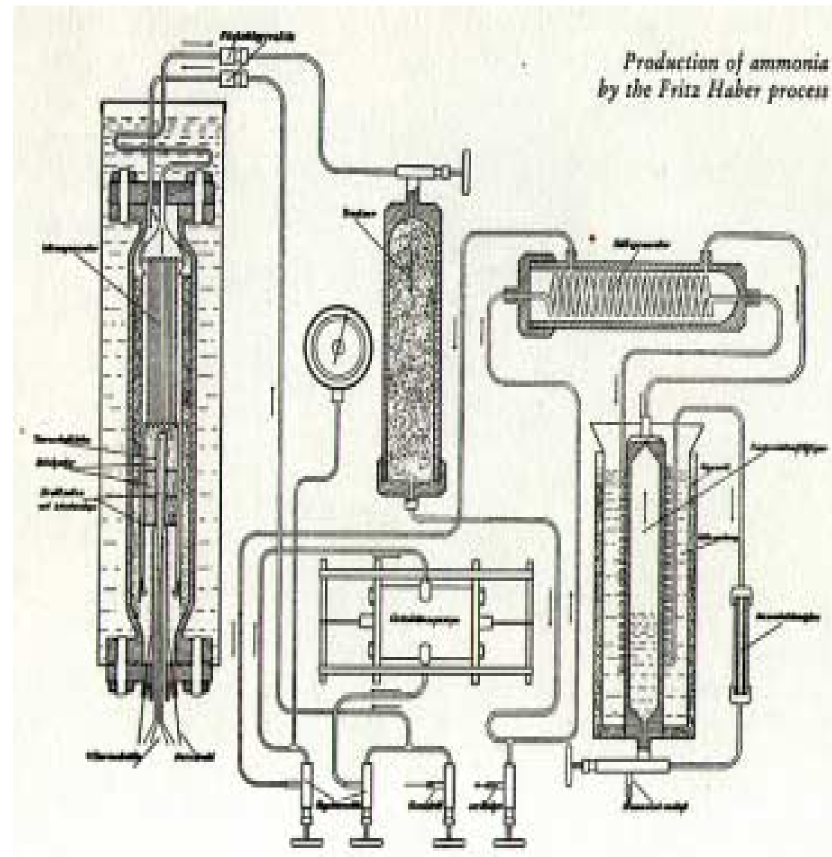
Haber Ammonia


PATENT-URKUNDE

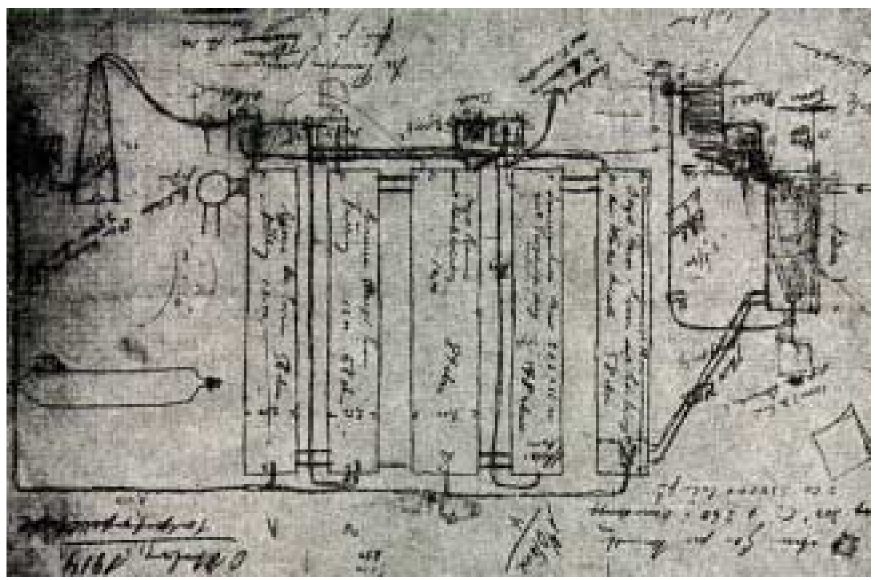
EIN PATENT ERTEILT WORDEN.

GEGENSTAND DES PATENTES IST:

KAISERLICHES PATENTAMT.



C. Bosch F. 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

$$N_2O_4\,(g,\text{red}) \Leftrightarrow 2NO_2\,(g,\text{colorless})$$

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{\left[\frac{2\alpha}{(1+\alpha)}P_T\right]^2}{\left[\frac{(1-\alpha)}{(1+\alpha)}P_T\right]}P_T = \frac{4\alpha^2}{1-\alpha^2}P_T$$

N_2O_4 (g,red) ⇔ $2NO_2$ (g,colorless)

- 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 Kp = 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

- $COCl_2(g) \Leftrightarrow CO(g) + Cl_2(g)$
  - 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 $\Delta n \neq 0$

$$NH_4HS(s) \Leftrightarrow NH_3(g) + H_2S(g)$$

- If Kp = 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.