A BRIEF HISTORY OF CATALYSIS

Who'sWho in the Early Catalysis

(Continued)

Jacobus Henricus van't Hoff, Jr. (1852-1911)

☐ born in Rotterdam, Netherlands
☐ Prof. at Prussian Academy of Sciences in Berlin ("University of Berlin")
☐ 1st Nobel Prize in Chemistry (1901)

"very dilute solutions follow mathematical laws applicable to the behavior of gases"

☐ physical justification for the Arrhenius equation (1889)
☐ **van 't Hoff equation** proposed in "Études de dynamique chimique" (Studies in Dynamic Chemistry) in 1884

$$\left(\frac{\partial \ln K}{\partial T} \right)_p = \frac{\Delta H}{RT^2}$$
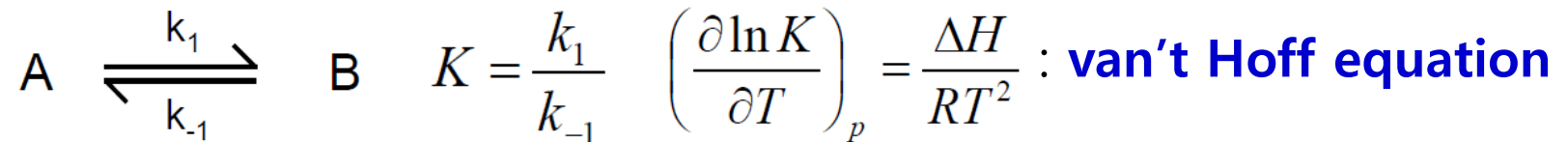
Svante August Arrhenius (1859-1927)

☐ Swedish chemist and physicist

☐ Nobel Prize in Chemistry 1903
"in recognition of the extraordinary services he has rendered to the advancement of chemistry by his electrolytic theory of dissociation"

☐ the greenhouse effect by an increases in atmospheric carbon dioxide,
Arrhenius equation,
Theory of ionic dissociation,
Acid-base theory

$$k = A \exp\left[-\left(\frac{E_a}{RT}\right)^{\beta}\right] \quad , \quad \beta = 1$$

Arrhenius equation

☐ a reaction between molecules A and B,

$$A \; \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \; B \qquad K = \frac{k_1}{k_{-1}} \qquad \left(\frac{\partial \ln K}{\partial T} \right)_p = \frac{\Delta H}{RT^2} \; : \textbf{\textcolor{blue}{van't Hoff equation}}$$

$$\left(\frac{\partial \ln k_1}{\partial T} \right) - \left(\frac{\partial \ln k_{-1}}{\partial T} \right) = \frac{\Delta H}{RT^2} \quad \left(\frac{\partial \ln k_1}{\partial T} \right) = \frac{E_1}{RT^2} \quad \left(\frac{\partial \ln k_{-1}}{\partial T} \right) = \frac{E_{-1}}{RT^2}$$

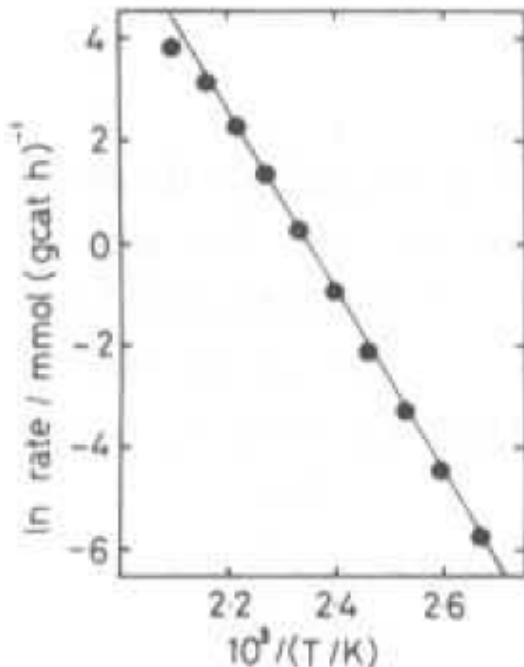$$\therefore \; E_1 - E_{-1} = \Delta H$$

☐ to calculate E_1 and E_{-1},

$$\ln k = \ln A - \frac{E_A}{RT}$$

- plot a ln k vs. 1/T

(Continued)

☐ as a rule of thumb, a rate of the reaction becomes doubling every 10 K increasing in temperature

☐ as an example, a hydrogenolysis of n-butane over a 1% Ru/Al_2O_3 catalyst in a flow of H_2 takes place.

(i) if only a single slop,
   only a single reaction pathway!

(ii) if two different slops,
   an indication of changes in
   reaction mechanism or from
   reaction to diffusion controls

Other dependence of k on T

☐ Berthelot (1862)

$$K = Ae^{DT} \qquad \ln k = \ln A + DT$$

☐ Harcourt and Esson (1895)

$$K = AT^{C} \qquad \ln k = \ln A + C \ln T$$

Walther Hermann Nernst (1864-1941)
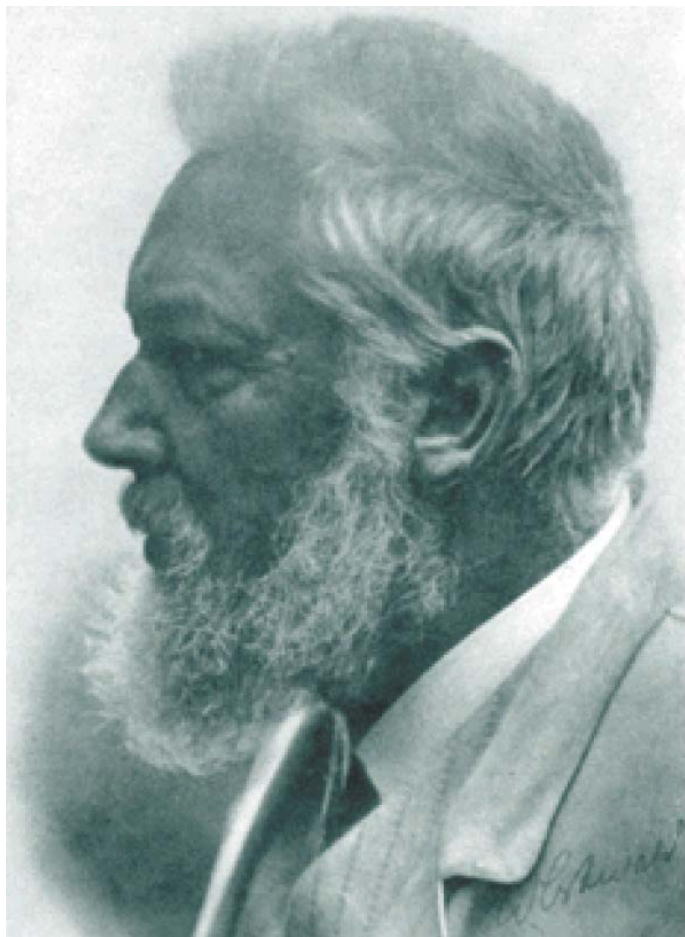

☐ **developed the third law of thermodynamics (1906-1912)** "Nernst (heat) theorem"

$$S - S_o = k_B \ln\Omega$$

the entropy of a perfect crystal of a pure substance ~ zero @ T = 0

☐ **The Nobel Prize in Chemistry (1920)**

☐ **developed Nernst equation (1887)**

☐ **a mathematical formalism between the rate of a reaction and the temperature and pressure of the reaction**

Friedrich Wilhelm Ostwald (1853-1932)

☐ Prof. of the Physical Chemistry

@ Leipzig and Harvard Univ. later

☐ **Catalytic process of NH$_3$ oxidation**

to nitric acid (1902),

"Ostwald process"

☐ **The Nobel Prize (1909)**

recognition on catalysis and fundamental principles governing chemical equilibria and rates of reaction

☐ **"Journal of Physical Chemistry" (1887)**

Ostwald's definition catalysis (1894)

☐ in reply to a definition by Stohmann (Z. Biol. 31 (1894) 364-391)

☐ "catalysis is the acceleration of a slowly proceeding chemical reaction through the presence of a foreign substance"

☐ "the acceleration occurs without a change of the energetic situation"

☐ "at the end of the reaction the foreign substance can be considered as removed"

W. Ostwald, Z. Phys. Chem. 15 (1894) 705-706

Paul Sabatier (1854-1941)

☐ French chemist
☐ **hydrogenating organic compounds in the presence of metals**
☐ great advance in the progress of organic chemistry
☐ **The Nobel Prize (1912)** together with V. Grignard
☐ **Sabatier reaction (or Sabatier process)** with Ni metals @ high Ts and Ps

◌ **$CO_2 + 4H_2 \rightarrow 2H_2O + CH_4$**
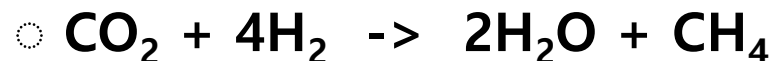
The International Space Station is using for the necessary water.

◌ **$CO + 3H_2 \rightarrow CH_4 + H_2O$ (SNG)**

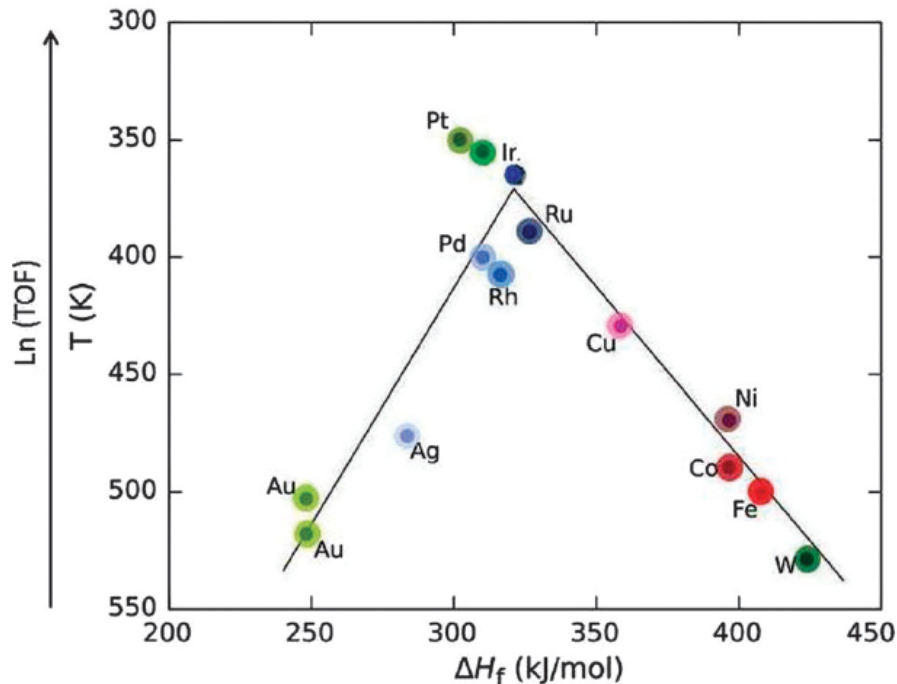# Sabatier principle of catalysis

□ **the interaction between a catalyst and a substrate should be:**

"**neither too strong nor too weak**"

□ a "**volcano plot**" of the decomposition of formic acid on transition metals

by A.A. Balandin

@ N.D. Zelinsky Institute of Organic Chemistry of the Academy of Sciences of the USSR, Moscow State University, Moscow

Fritz Haber (1868-1934)

☐ **opened the way of the conversion of atmospheric N_2 to NH_3**

☐ **commercialized "Haber-Bosch process"**

Ammonia synthesis using the Haber process on an industrial scale in 1913 in BASF's Oppau plant

☐ **The Nobel Prize (1918)**

☐ **"Journal of Physical Chemistry" (1887)**

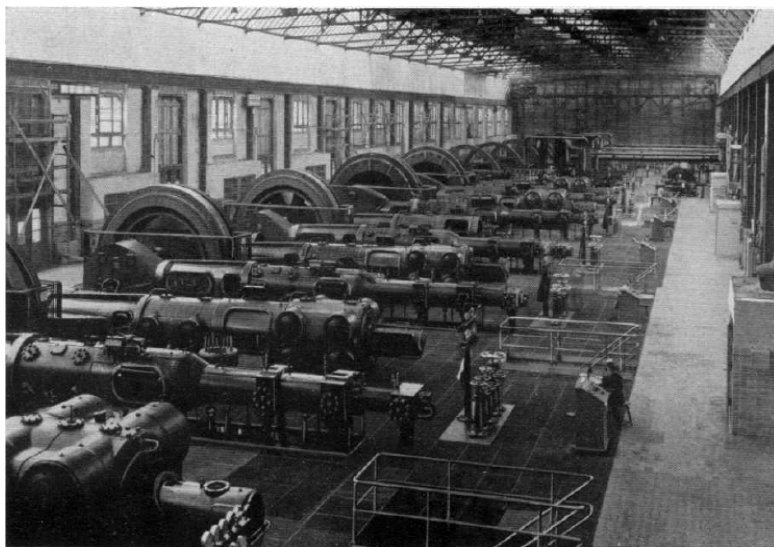# "The Father of Chemical Weapons"

Haber (pointing) instructs soldiers about chlorine gas deployment in WWI.

Clara Immerwahr (1870–1915): the first woman of PhD in chemistry in Germany

Ammonia synthesis

$$N_2 + 3H_2 = 2NH_3$$

Kompressor-Anlage
Werk Oppau

☐ measurements of the equilibrium
(Haber, 1904/05)

☐ experiments with high pressure
by Le Chatelier

☐ Nernst's suggestion to Haber: use high
pressure

☐ **osmium as a first catalyst (1909)**

   - by 1912: 6500 tests with 2500 catalysts
   - by 1919: 10000 tests 4000 catalysts

☐ **Fe/K catalyst**

Carl Bosch (1874-1940)

☐ **worked with Haber**

☐ **commercialized "Haber-Bosch process"**

Ammonia synthesis using the Haber process on an industrial scale in 1913 in BASF's Oppau plant

☐ **The Nobel Prize (1931) along with F. Bergius**

"the invention and development of chemical high pressure methods"

Irving Langmuir (1881-1957)

☐ **worked with Nernst**
☐ Researcher at General Electric
☐ **The Nobel Prize (1932)**

   "for discoveries and investigations in surface chemistry"

☐ The journal **"Langmuir" (1985)** established by ACS
☐ **Langmuir adsorption and isotherm: 1st quantitative theory of adsorption**

Fraction Adsorbed →   Equilibrium constant ↓   Equilibrium Pressure ↙

$$\theta = \frac{KP}{KP+1}$$

Hugh Stott Taylor (1890-1974)

☐ Prof. of Physical Chemistry in Princeton

☐ a small amount of CO adsorbed on quartz:

"only a small fraction of the surface is active"

☐ "the amount of surface which is catalytically active is determined by the reaction catalyzed"

☐ **a concept of "active sites"/"centers"**

☐ **1st detailed theory of contact catalysis**

Karl Waldemar Ziegler (1898-1973)
Giulio Natta (1903-1979)

☐ "for discoveries in the field of the chemistry and technology of high polymers"

☐ **Nobel Prize in Chemistry (1963)**