Entropy, S

Natural processes have a preferred direction of progress, systems tend to progress in the direction of increasing entropy

Entropy
= a measure of the number of ways in which a system may be arranged
= a measure of accessible energy levels
= a measure of thermal effects of reversible processes

Reversible processes = a small change in conditions could reverse the direction

Irreversible processes

Spontaneous Processes

Proceed in a given direction without being driven by an outside source of energy

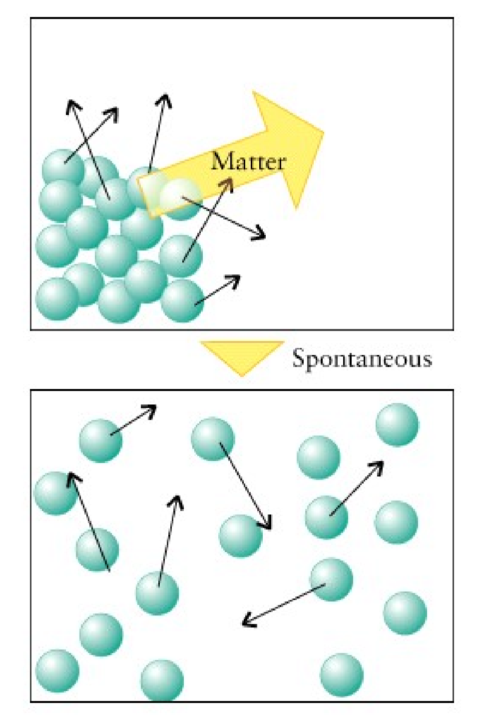
Increase entropy S of Universe

Proceed in a direction towards states with highest probabilities

Lead to disipitation of energy

Spontaneous Processes

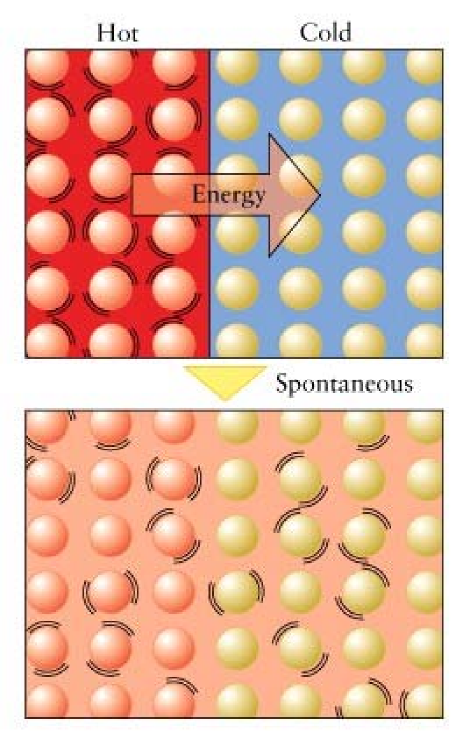
Expansion of gas



$\Delta S = R \ln V_{fin}/V_{init}$
(1 mol of ideal gas)

Spontaneous

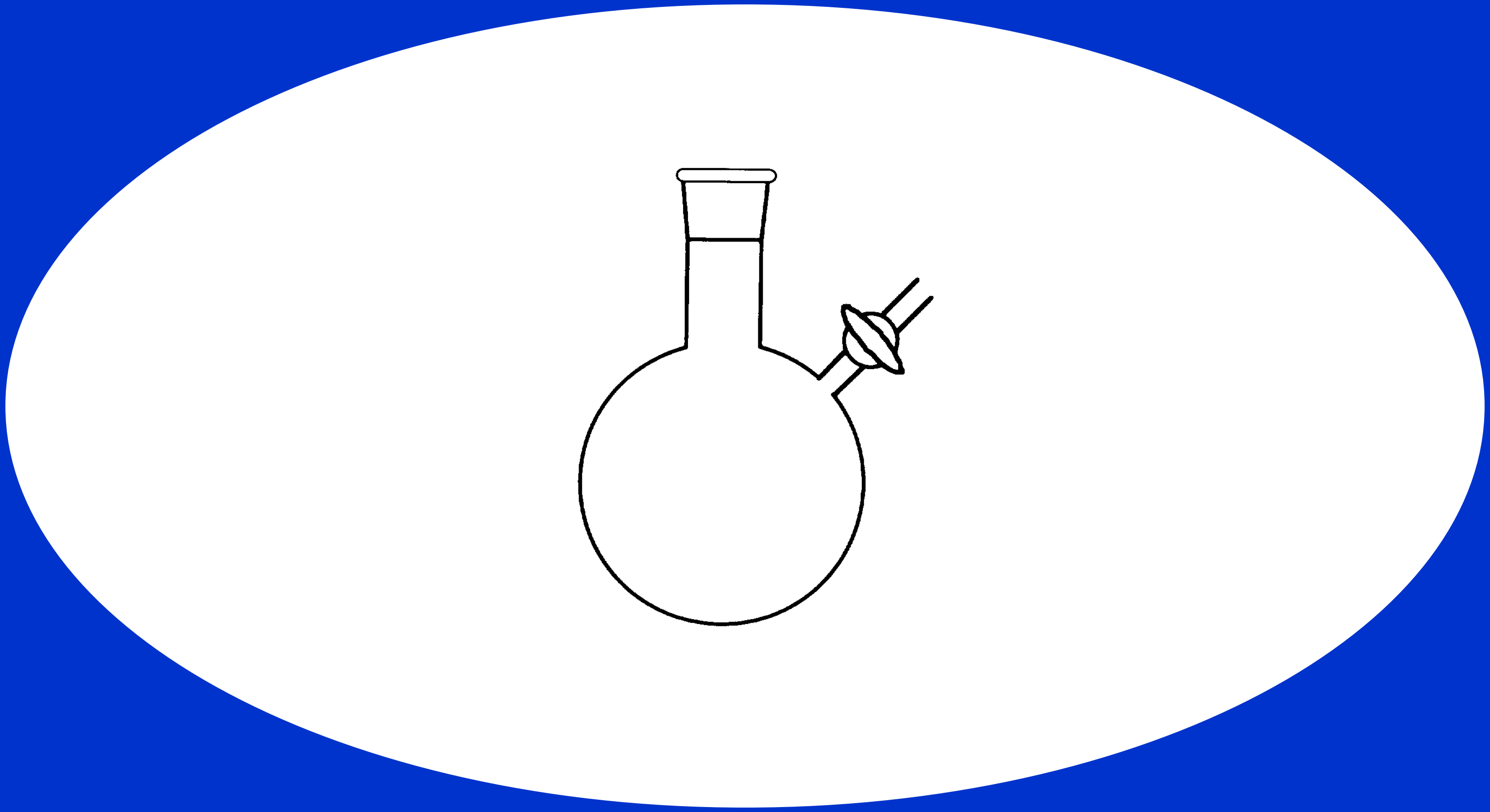
Heat transfer



$\Delta S = C_p \ln T_2/T_1$

Universe, System, Surroundings

Universe = System + Surroundings



Second Law of Thermodynamics

Entropy of universe increases
Spontaneous processes increase entropy of universe

$$\Delta S_{univ} = \Delta S_{syst} + \Delta S_{surr}$$

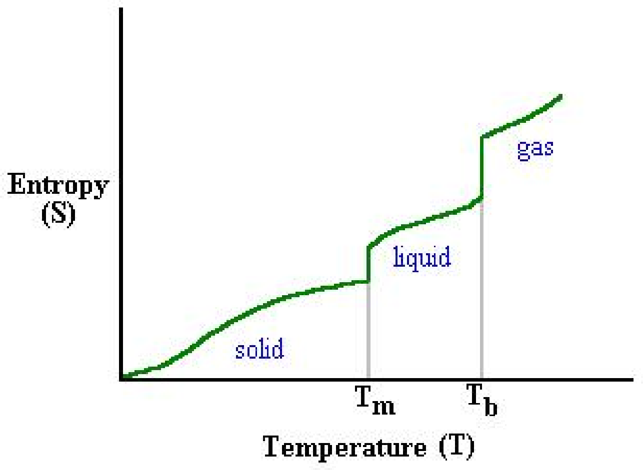
$\Delta S_{univ} > 0$ Spontaneous processes

$\Delta S_{univ} < 0$ Process does not proceed in given direction

$\Delta S_{univ} = 0$ Equilibrium

To establish spontaneity of a process, we need to know ΔS_{syst} and ΔS_{surr}

Third Law of Thermodynamics



Entropy of ideal crystal at 0 K equlas **zero**

- ideal crystal does not exist
- 0 K cannot be attained

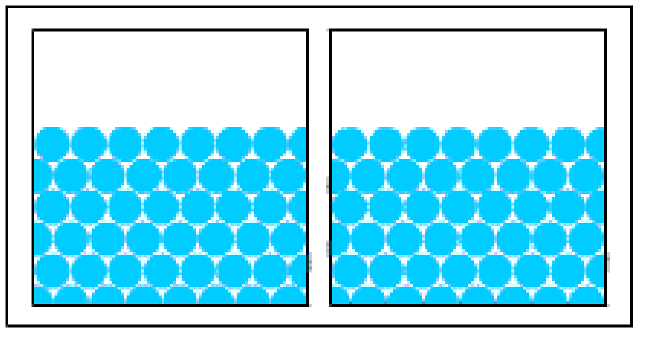
Reference state – perfect ordering

– motions, vibrations, rotations ceased

S = k ln W

W = number of microstates of a system

At 0 K W = 1, S = 0



Boltzmann Equation

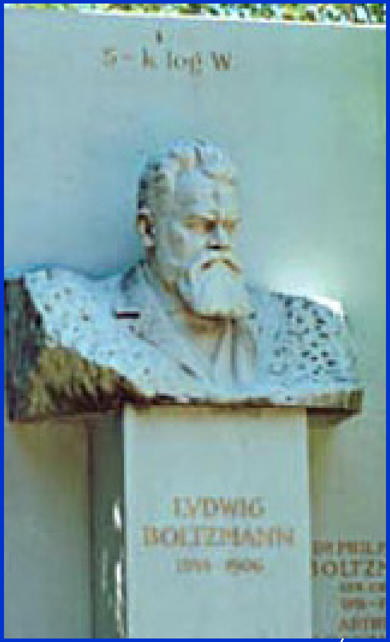
Ludwig Edward Boltzmann

$S = k \ln W$

$k = R/N_A = 1.38066\ 10^{-23}\ J\ K^{-1}$

W = number of microstates of a system

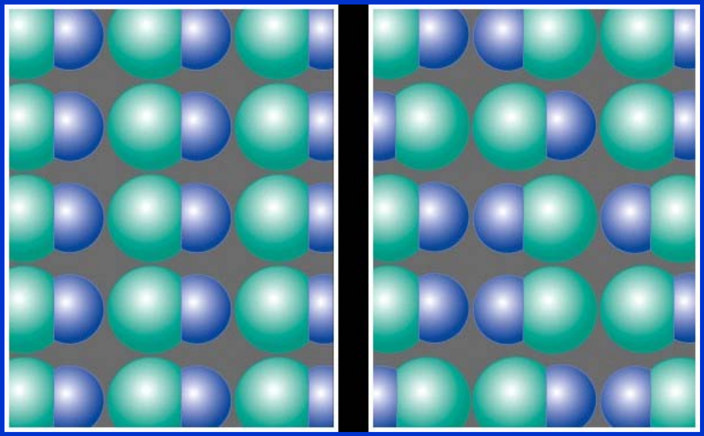
It is possible to establish value of S for a given state
(in contrast to H or U)



On October 5, 1906 committed suicide in Duinu by Trieste

Boltzmann Equation

$$S = k \ln \frac{W_{fin}}{W_{init}}$$



T = 0

W_{init} = 1

S = 0

T = 273 K

W_{fin} = ?

S = 41 J K^{-1}

k = Boltzmann constant = $1.3807\ \ 10^{-23}$ J K^{-1}

W = number of microstates of a system

$\ln W_{fin} = S / k = 41 / 1.3807\ \ 10^{-23} = 10^{24}$

Standard Entropy

S^0 = Standard molar entropy of a substance látky
at 298 K and 1 bar

(increase of S on heating a substance from 0 K to 298 K)

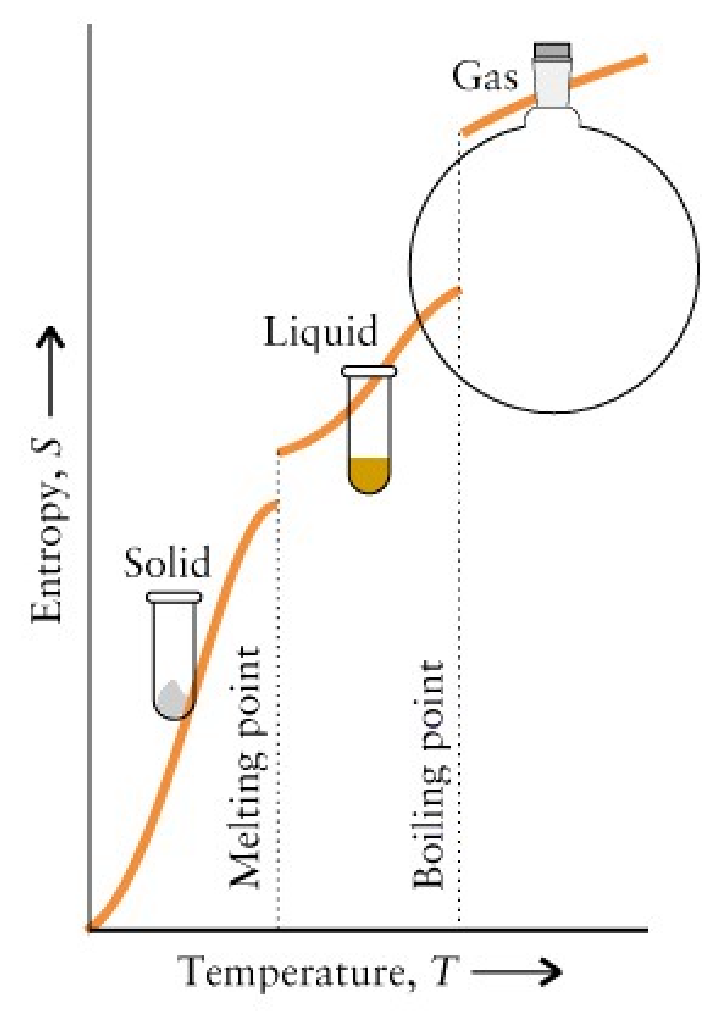
$S^0 = \Delta S = S\ (298\ K) - S\ (0\ K)$

$J\ mol^{-1}\ K^{-1}$

Standard Entropies S^0 at 298 K and 1 bar

Substance	S^0, J K^{-1} mol^{-1}	Substance	S^0, J K^{-1} mol^{-1}
S_8 (g)	431	H_2O (g)	189
SF_6 (g)	292	H_2O (l)	70
O_2(g)	205	H_2O (s)	41
CO_2(g)	248	$CaCO_3$(s)	93
CO(g)	198	CaO(s)	40
H_2 (g)	131	Sn (s) white	52
CH_3OH (g)	240	Sn (s) gray	44
CH_3OH (l)	127	C(s) graphite	6
C_2H_5OH (l)	161	C(s) diamond	2

Standard Entropies S^0



Entropy decreases : g > l > s

Substance	S^0, J K^{-1} mol^{-1}
H_2O (g)	189
H_2O (l)	70
H_2O (s)	41
Na (g)	153
Na (s)	51

Standard Entropies S^0

Dissolution

Substance	S^0, J K^{-1} mol^{-1}
CH_3OH (l)	127
CH_3OH (aq)	133
NH_4Cl (s)	94
NH_4Cl (aq)	168

Standard Entropies S^0

Molecular mass, number of atoms in a molecule, number of vibrations and rotations

Substance	S^0, J K^{-1} mol^{-1}
K (g)	160
Cl_2 (g)	223
P_4 (g)	280
As_4 (g)	289

Substance	S^0, J K^{-1} mol^{-1}
F_2 (g)	203
Cl_2 (g)	223
Br_2 (g)	245
I_2 (g)	260

Heavy molecules – energy levels close spaced, more available states

Standard Entropies S^0

Chemical composition

More complicated molecules

Substance	S^0, J K^{-1} mol^{-1}
NaCl (s)	74
$MgCl_2$ (s)	90
$AlCl_3$ (s)	167

Standard Entropies S^0

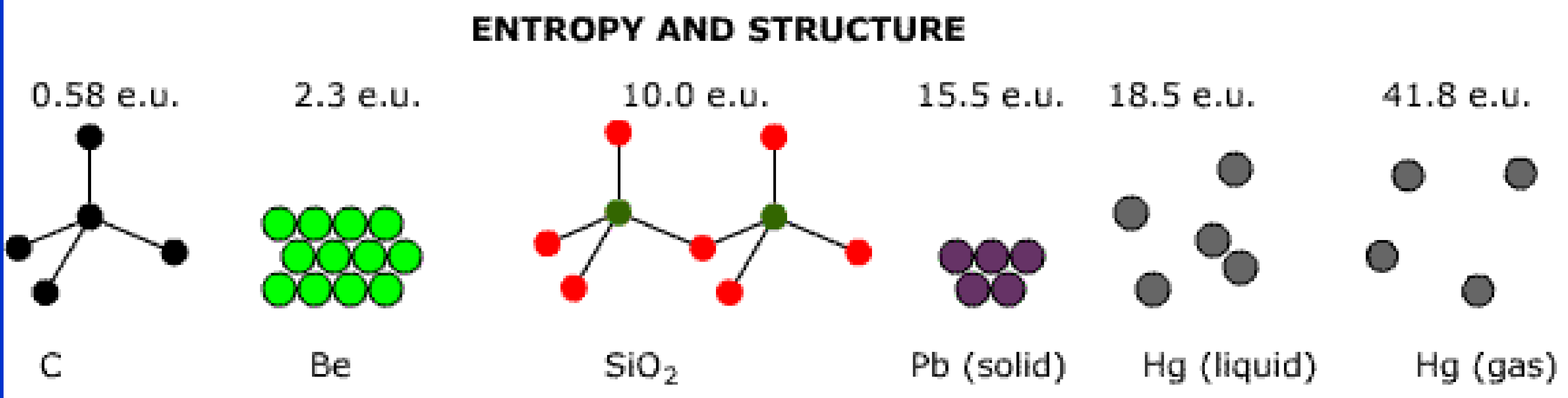
Strong covalent bonds – low entropy

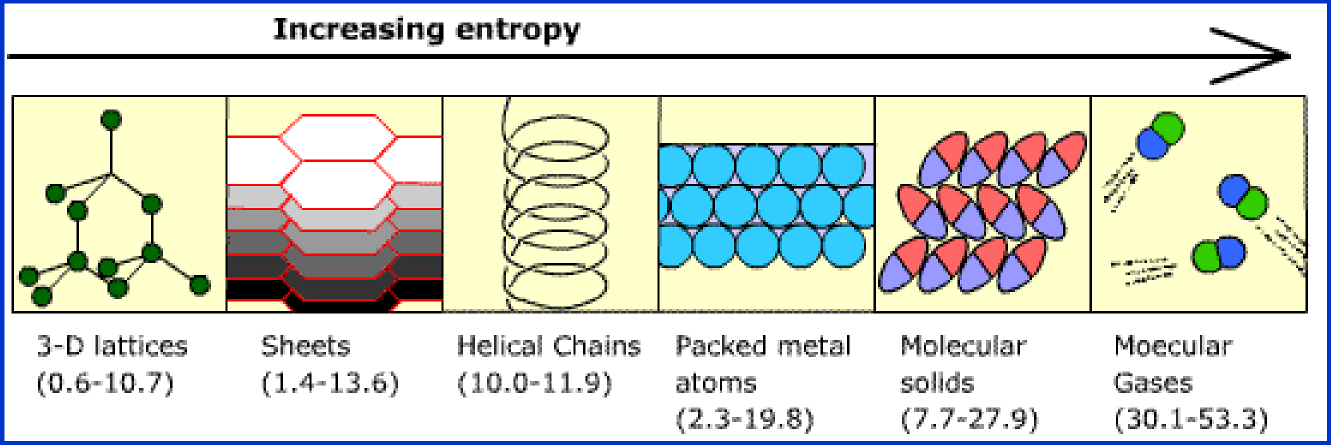
Entropy increases:

3D < 2D < 1D < 0D structures

Substance	**S^0, J K^{-1} mol^{-1}**
Sn (s) white	**52**
Sn (s) gray (diamond)	**44**
C(s) graphite, 2D	**6**
C(s) diamond, 3D	**2**
P_4 (s) white, 0D	**44**
P_4 (s) black, 2D	**29**

Standard Entropies S^0





Reaction Entropy

$$\Delta S^0_r = \Sigma\, n_{prod}\, S^0_{prod} - \Sigma\, n_{react}\, S^0_{react}$$

Products – Reactants

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$

$\Delta S^o_r = [2(69.9) + 213.6] - [182.6 + 2(205.0)] = -242.8\ J\ K^{-1}$

$\Delta S^0_r < 0$ for reactions:

Formation of solids or liquids from gases

Total number of moles of gases decresas

$\Delta S^0_r > 0$ for reactions:

Formation of gases from solids or liquids

Total number of moles of gases incresas

Second Law of Thermodynamics

Entropy of universe increases
Spontaneous processes increase entropy of universe

$$\Delta S_{\mathbf{univ}} = \Delta S_{\mathbf{syst}} + \Delta S_{\mathbf{surr}}$$

$\Delta S_{\text{univ}} > 0$ Spontaneous processes

$\Delta S_{\text{univ}} < 0$ Process does not proceed in given direction

$\Delta S_{\text{univ}} = 0$ Equilibrium

To establish spontaneity of a process, we need to know ΔS_{syst} and ΔS_{surr}

Heat Exchange between System and Surroundings

$$\Delta S_{surr} = \frac{-\Delta H_{syst}}{T}$$

At p = const

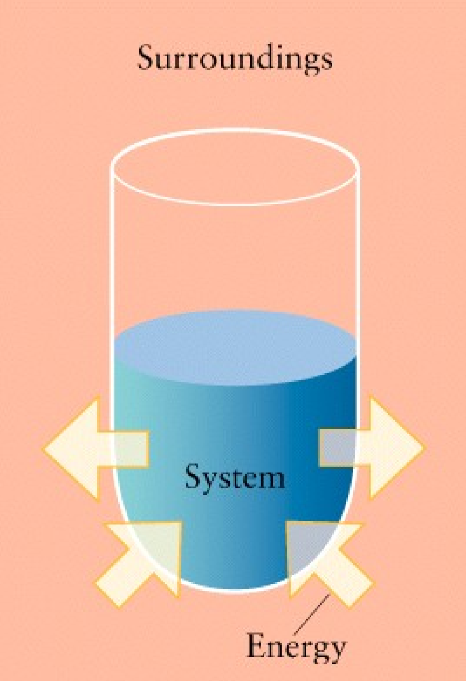
Heat (surr) = – ΔH (system)

Given off $(+)$ Lost $(-)$

Removed $(-)$ Absorbed $(+)$

We can establish ΔS_{surr}

ΔH	ΔS_{surr}
< 0 exo	> 0 incr
> 0 endo	< 0 decr



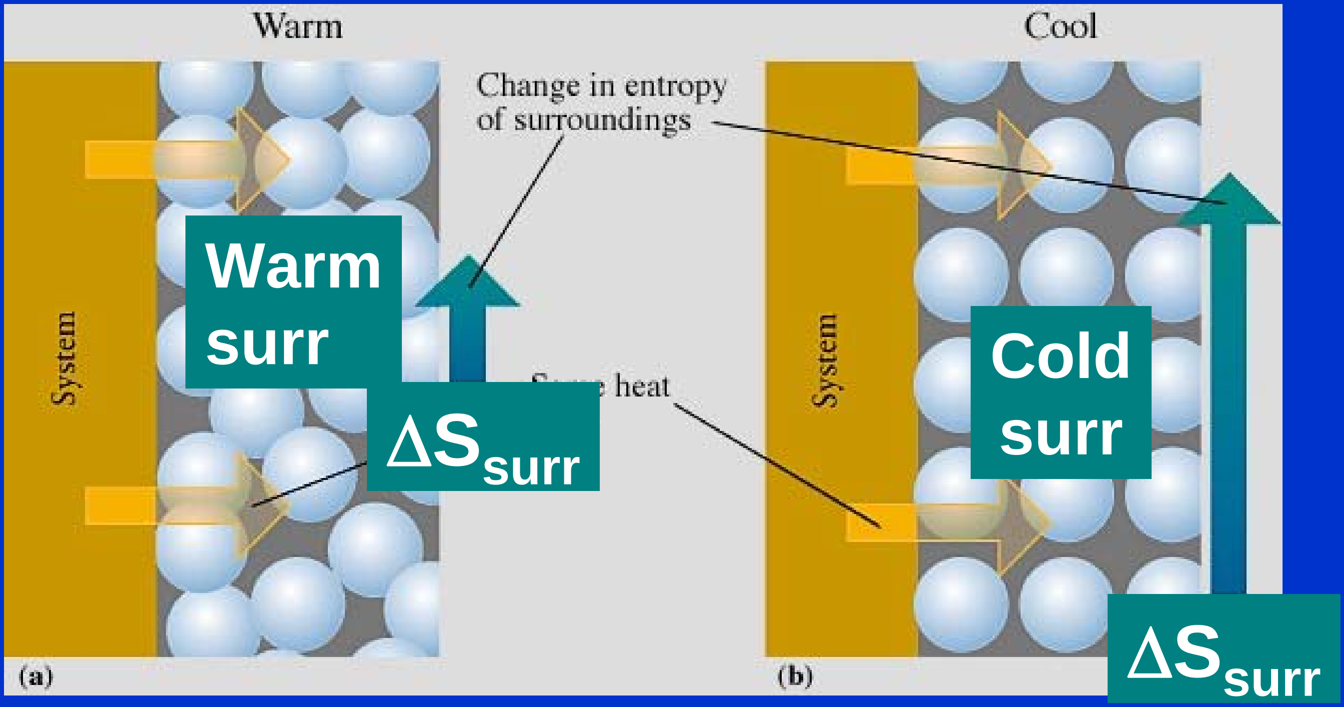
At 298 K

$Sb_4O_6(s) + 6C(s) \rightarrow 4Sb(s) + 6CO_2(g)$ $\Delta H = 778$ kJ

$\Delta S_{surr} = -\Delta H/T = -778 \text{ kJ} / 298 \text{ K} = -2.6 \text{ kJ K}^{-1}$

$$\Delta S_{surr} = \frac{-\Delta H_{syst}}{T}$$

Heat Exchange



Transfer of the same amount of heat at lower temperature increases relatively more entropy of surroundings – cold surroundings are more ordered and then more disturbed

Reaction Entropy

$$2Fe(s) + 3H_2O(g) \rightarrow Fe_2O_3(s) + 3H_2(g)$$

$$\Delta S°_r = [S°(Fe_2O_3(s) + 3S°H_2(g)] - [2S°Fe(s) + 3S°H_2O(g)]$$

$$\Delta S°_r = -141.5 \text{ J K}^{-1}$$

Is this reaction spontaneous at 298 K, is $\Delta S°_{univ} > 0$?

$$\Delta S_{univ} = \Delta S_{syst} + \Delta S_{surr}$$

$$\Delta S°_r = \Delta S°_{syst} = -141.5 \text{ J K}^{-1}$$

Reaction Spontaneity

$$\Delta S°_{surr} = -\Delta H°_{syst}/T = -\Delta H°_r/T$$

$$\Delta H°_r = \Delta H°_f(Fe_2O_3(s)) + 3\Delta H°_f(H_2(g)) - 2\Delta H°_f(Fe\,(s)) - 3\,\Delta H°_f(H_2O(g)) = -100\text{ kJ}$$

$$\Delta S°_{surr} = -\Delta H°_{syst}/T = 336\text{ J K}^{-1}$$

$$\Delta S°_{univ} = \Delta S°_{syst} + \Delta S°_{surr}$$
$$= -141.5 + 336 = 194.0\text{ J K}^{-1}$$

Reaction is spontaneous at 298 K, $\Delta S°_{univ} > 0$

Entropy of Phase Transitions

$H_2O(l) \leftrightarrows H_2O(g)$ at 373 K

$$\Delta S^0_{surr} = \frac{-\Delta H_{vap}}{T_b}$$

$H_2O(s) \leftrightarrows H_2O(l)$ at 273 K

$$\Delta S^0_{surr} = \frac{-\Delta H_{melt}}{T_m}$$

Entropy of Phase Transitions

$H_2O(l) \leftrightarrows H_2O(g)$ při 373 K

Phase Transitions are **equilibrium** processes
at which $\Delta S°_{\mathbf{univ}} = \mathbf{0}$

$\Delta S°_{syst} = S°(H_2O(g)) – S°(H_2O(l)) = 195.9\ J\ K^{–1} – 86.6\ J\ K^{–1}$
$= 109.1\ J\ K^{–1}$

$H_2O(l)$ 1 mol = 18 g ~ 18 cm^3
$H_2O(g)$ 1 mol = 31 liter at 100 °C

$\Delta S°_{surr} = –\Delta H_{vap} / T = –40.7\ kJ/373\ K = –109.1\ J\ K^{–1}$

$\Delta S°_{univ} = \Delta S°_{syst} + \Delta S°_{surr} = 0$

Second Law of Thermodynamics

$$\Delta S_{univ} = \Delta S_{syst} + \Delta S_{surr}$$

$$\boxed{\Delta S_{univ} = \Delta S_{syst} + \frac{-\Delta H_{syst}}{T}}$$

Spontaneous Processes and Gibbs Energy

Reaction is spontaneous when $\Delta S_{univ} > 0$

$$\Delta S_{univ} = \Delta S_{syst} + \Delta S_{surr} = \Delta S_{syst} - \Delta H_{syst}/T > 0$$

Multiply by $-T$

Multiply by –1 reverse unequal.

$$\underbrace{\Delta H - T\Delta S_{syst}} < 0$$

$\Delta G \equiv$ **Gibbs Free Energy** $(= - T\Delta S_{univ})$

$$\mathbf{\Delta G = \Delta H_{syst} - T\Delta S_{syst}}$$

When ΔG is negative, reaction is spontaneous !

Gibbs Free Energy

1. ΔG is a state function
2. ΔG° Gibbs Free Energy at standard cond.
   - 298 K
   - 1 bar for gases
   - 1 mol l^{-1} concentration
3. ΔG° tabulated

$$1/2O_2\,(g) + N_2(g) \leftrightarrows N_2O\,(g)$$

$$\Delta G^\circ_f\,(N_2O) = 104.18\ \text{kJ mol}^{-1}$$

Reactants are more stabile than products
Kinetic factors of N_2O stability

Standard Gibbs Free Energy of Formation

$\Delta G°_f$ calculated from $\Delta H°_f$ and S°

$C(graphite) + O_2(g) \leftrightarrows CO_2(g)$

$\Delta H°_f = \Delta H_r° = – 393.5\ kJ\ mol^{-1}$

$\Delta S° = S° (CO_2(g)) – S° (C(graphite)) – S° (O_2(g))$

$\Delta S° = 213.60 – 5.74 – 205.00 = 2.86\ J\ K^{-1}\ mol^{-1}$

$\Delta G°_f = \Delta H°_f – T\Delta S°_f$

$\Delta G°_f = –393.5 – (298)(2.86) = – 394.360\ J\ K^{-1}\ mol^{-1}$

Standard Gibbs Free Energy of Formation

(at 25 °C)

ΔG°_f

Substance	ΔG°_f, kJ mol^{-1}
NH_3	– 16.45
CO_2	– 394.4
NO_2	+ 51.3
H_2O (g)	– 228.6
H_2O (l)	– 237.1
C_6H_6	+ 124.3
C_2H_5OH	– 174.8
AgCl	– 109.8
$CaCO_3$	– 1128.8

ΔG^0_r Calculated from ΔG_f^0

$$\Delta G^0_r = \Sigma\, n_{prod}\, \Delta G^0_f\,(prod) - \Sigma\, n_{react}\, \Delta G^0_f\,(react)$$

$$aA + bB \leftrightarrows cC + dD$$

$$\Delta G^0 = c\Delta G^0_f\,(C) + d\Delta G^0_f\,(D) - a\Delta G^0_f\,(A) - b\Delta G^0_f\,(B)$$

$$3NO(g) \leftrightarrows N_2O(g) + NO_2(g) \qquad \Delta G^0 = ?$$

$$\Delta G^0 = \Delta G^0_f\,(N_2O) + \Delta G^0_f\,(NO_2) - 3\Delta G^0_f\,(NO)$$

$$\Delta G^0_r = 104.18 + 51.29 - 3(86.55) = -104\ kJ\ mol^{-1}$$

Influence of Temperature on ΔG^0

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0$$

ΔH^0 +	ΔS^0 +	ΔG^0 Negative at high T
ΔH^0 +	ΔS^0 –	ΔG^0 Positive at all T
ΔH^0 –	ΔS^0 +	ΔG^0 Negative at all T
ΔH^0 –	ΔS^0 –	ΔG^0 Negative at low T

Chemical Equilibria

C. L. Berthollet
(1748-1822)

In laboratory

$Na_2CO_3 + CaCl_2 \rightarrow CaCO_3 + 2\ NaC$

Natron on banks of salt lakes in Egypt

$CaCO_3 + 2\ \mathbf{NaCl} \rightarrow Na_2CO_3 + CaCl_2$

An excess of a product can reverse the course of chemical reaction

Reversibile reaction

$Na_2CO_3 + CaCl_2 \rightleftharpoons CaCO_3 + 2\ NaCl$

Reaction Quotient Q

Reversibile reaction : aA + bB ⇆ cC + dD

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

Unequilibrium concentrations powered to stoichiometric coefficients

Q = Reaction quotient

How far a reaction proceeded from reactants to products

At the start of reaction:

[A] = [B] = 1 M
[C] = [D] = 0

$Q = 0/1 \rightarrow 0$

A complete reaction:

[A] = [B] = 0
[C] = [D] = 1 M

$Q = 1/0 \rightarrow \infty$
(for $a = b = c = d = 1$)

Chemical Composition and ΔG

One of the most important equations in chemistry !

$$\Delta G = \Delta G^0 + RT \ln Q$$

Q = Reaction quotient

$$3NO(g) \leftrightarrows N_2O(g) + NO_2(g) \qquad \Delta G^0 = -104 \text{ kJ mol}^{-1}$$

$NO = 0.3$ atm ; $N_2O = 2$ atm ; $NO_2 = 1$ atm Which direction ?

$$Q_P = \frac{P_{N2O}P_{NO2}}{P_{NO}^3} = \frac{(2)(1)}{(0.3)^3} = 74.1$$

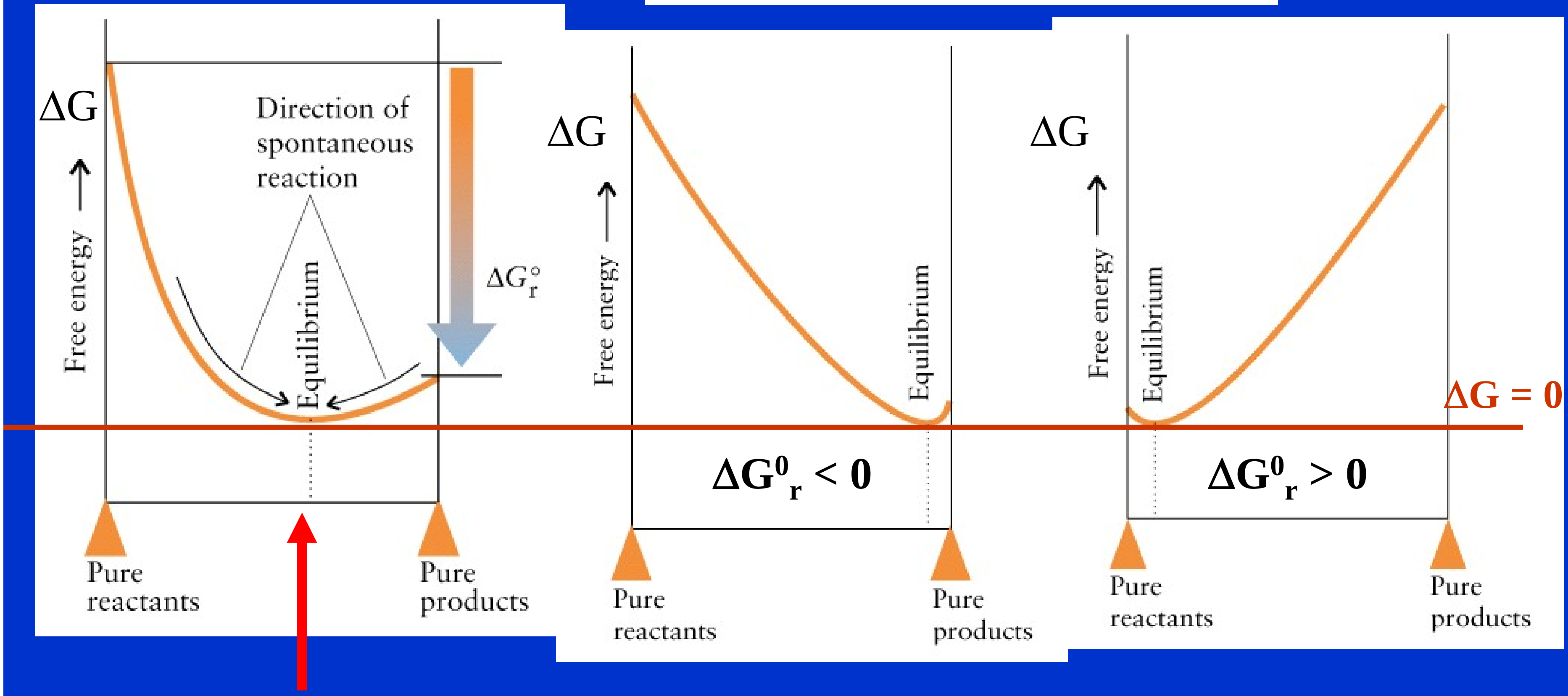
$$\Delta G = \Delta G^0 + RT \ln Q = -104.0 + (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) \ln (74.1)$$

$\Delta G = -93.3 \text{ kJ mol}^{-1}$ Reaction is spontaneous to the right
more NO decomposes to products

Chemical Composition and ΔG

$aA + bB \leftrightarrows cC + dD$

$$\boxed{\Delta G = \Delta G^0_r + RT \ln Q}$$



Q = K

At equilibrium ΔG = 0

ΔG^0 and Equilibrium Constant K

$\Delta G = \Delta G^0 + RT \ln Q$

At equilibrium $\Delta G = 0$ and $Q = K$

$$\boxed{\mathbf{\Delta G^0 = -RT \ln K}}$$

$$K = e^{-\frac{\Delta G^0}{RT}}$$

aA + bB ⇆ cC + dD

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

Equilibrium concentrations

Reaction Quotient Q and Equilibrium Constant K

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

Q = K. System at equilibrium, no change.

Q > K. Concentrations of products are larger then equilibrium concentrations. A part of the products must convert back to reactants to attain equilibrium. Reaction shift to the left.

Q < K. Concentrations of reactants are larger then equilibrium concentrations. A part of the reactants must react to products to attain equilibrium. Reaction shift to the right.

ΔG^0 and Equilibrium Constant K

$3NO(g) \leftrightarrows N_2O(g) + NO_2(g)$ $\Delta G^0 = -104$ kJ mol^{-1}

$$K = e^{-\frac{\Delta G^0}{RT}} = e^{\frac{-(-104{,}000)}{(8.314)(298)}} = 1.8\,x10^{18}$$

$$K = \frac{[NO_2]^1[N_2O]^1}{[NO]^3}$$

ΔG^0 and Equilibrium Constant K

$$\Delta G^0 = -RT \ln K$$

ΔG^0	**K**	At equilibrium ($\Delta G = 0$)
< 0	> 1	More products
> 0	< 1	More reactants
$= 0$	$= 1$	

Equilibrium Constant K

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

K is a function only of temperature
Pure phases (l, s) do not influence equilibrium
Concentration of solvent is not considered
K is dimensionless
Concentrations related to standard state 1 M

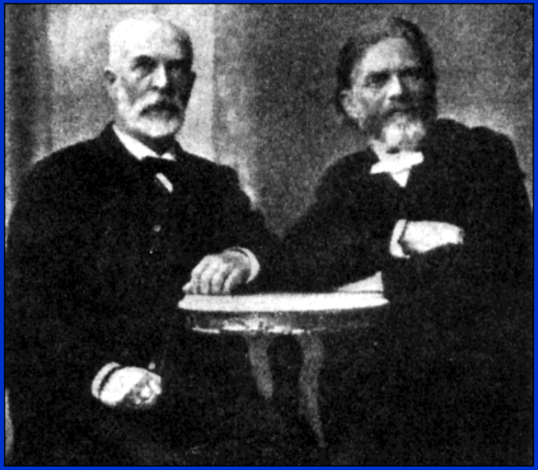
Guldberg-Waage Law

1864 Law of mass action

$$aA + bB \leftrightarrows cC + dD$$

K = Equilibrium Constant

$$K = \frac{[C]^c_{eq}[D]^d_{eq}}{[A]^a_{eq}[B]^b_{eq}}$$



Cato Maximilian Guldberg (1836-1902)

Peter Waage (1833-1900)

Guldberg-Waage Law

$cC + dD \leftrightarrows aA + bB$

Reverse reaction, $K_{new} = 1/K$

$ncC + ndD \leftrightarrows naA + nbB$

Multiply equation by a constant $K_{new} = (K)^n$

Sum of chemical equations

$K_{new} = K_1 \times K_2$

Guldberg-Waage Law

$2\ NO_2 \leftrightarrows 2\ NO + O_2$ K_1

$2\ SO_2 + O_2 \leftrightarrows 2\ SO_3$ K_2

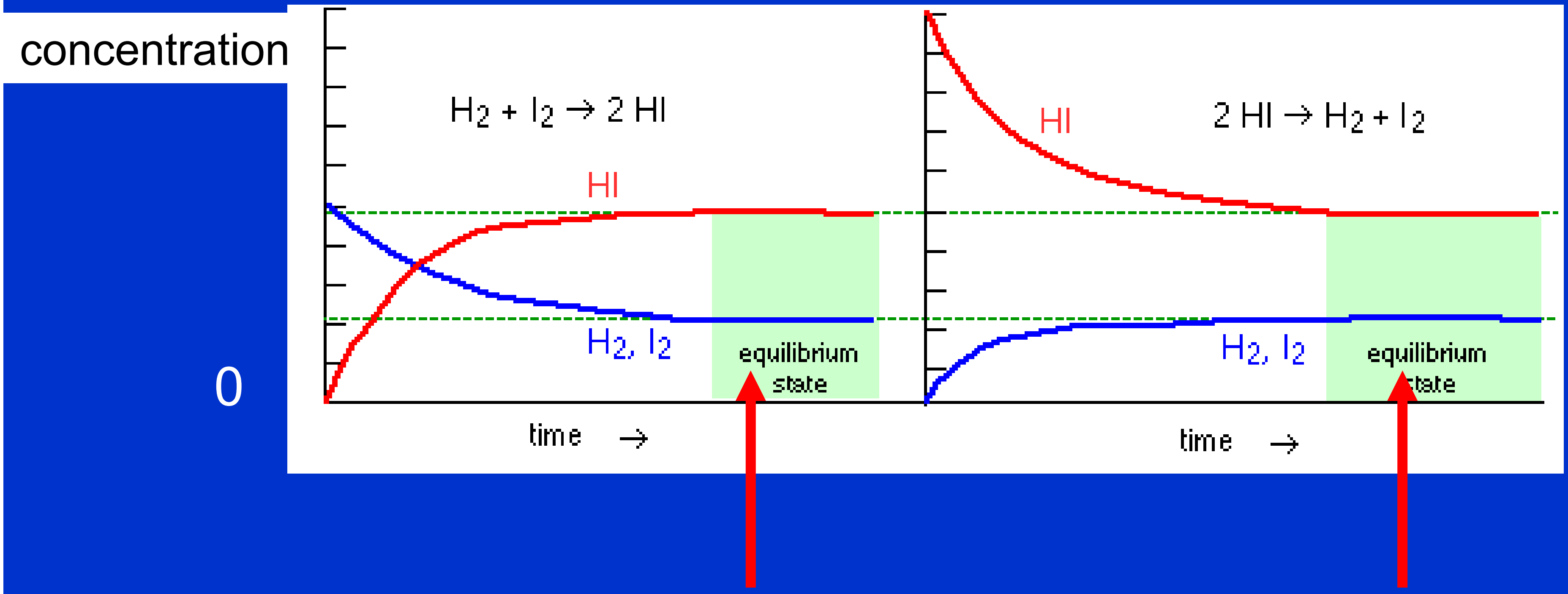
$NO_2 + SO_2 \leftrightarrows NO + SO_3$ $K_3 = ?$

$$K_3 = (K_1 \times K_2)^{1/2} = \sqrt{K_1 \times K_2}$$

Attaining Chemical Equilibrium

$H_2 + I_2 \rightarrow 2\,HI$

$2\,HI \rightarrow H_2 + I_2$



Equilibrium concentrations

Equilibrium concentrations

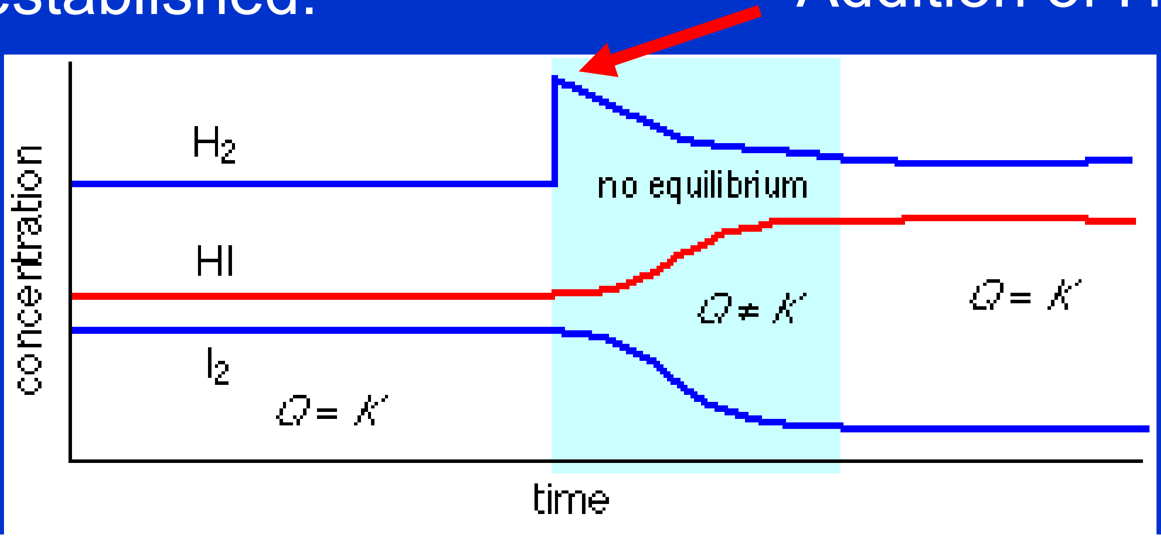
LeChatelier’s Principle

Reversibile reactions

If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, then the equilibrium shifts to counteract the imposed change and a new equilibrium is established.

Henri LeChâtelier
(1850-1936)

$$K_C = \frac{[HI]^2}{[H_2][I_2]}$$



Addition of H_2

Concentrations

K is const.

$CO_2\,(g) + H_2\,(g) \leftrightarrows H_2O\,(g) + CO\,(g)$

Trapping water, shift to right

$NaCl\,(s) + H_2SO_4\,(l) \leftrightarrows Na_2SO_4\,(s) + HCl\,(g)\uparrow$

Gaseous HCl escapes, shift to right

$H_2\,(g) + I_2\,(g) \leftrightarrows 2HI\,(g)$

Addition of inert N_2, does not take part in reaction, no change in number of moles, no shift

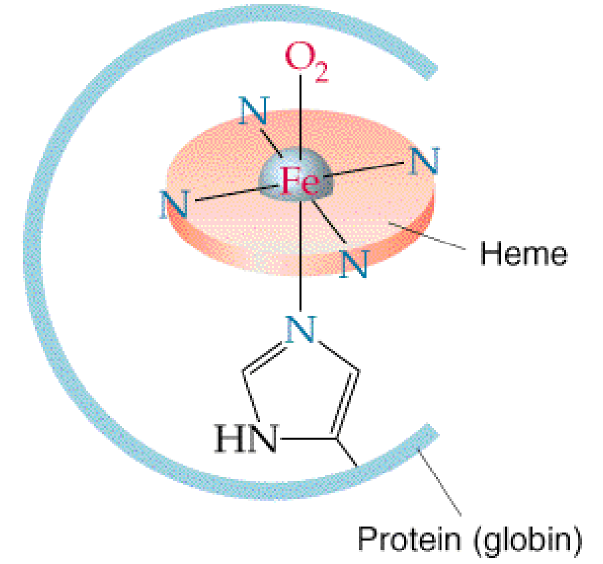
Transfer of Oxygen and CO_2

hemoglobin + O_2 ⇆ oxyhemoglobin

Fe^{2+} highspin Fe^{2+} lowspin

O_2-hemoglobin ⇆ hemoglobin ⇆ CO-hemoglobin

$H_2O + CO_2 + CO_3^{2-} \rightleftarrows 2\ HCO_3^-$



Pressure

Reactions with changing number of moles of gases

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

K is const.

$\Delta n_g = (n_{prod} - n_{react}) = 1 - 2 = -1$

V halved, p 2x bigger

$\leftarrow Q = \frac{1}{2} K_p \swarrow$

Increased pressure shifts reaction to the right

compress →

shift →

New equilibrium

Pressure

$N_2(g) + 3\ H_2(g) \leftrightarrows 2\ NH_3(g)\quad \Delta H = -92\ kJ\ mol^{-1}$

- the reaction is exothermic
- decreasing number of moles of gases

Fritz Haber

(1868-1934)

NP in Chemistry 1918

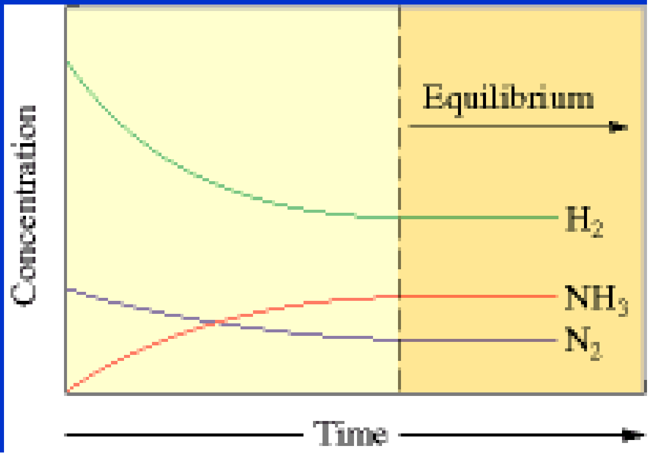
According to LeChatelier, the yield will be at maximum at high pressure and low temperature

At low temperature, the reaction is slow

uses Fe catalyst to speed up

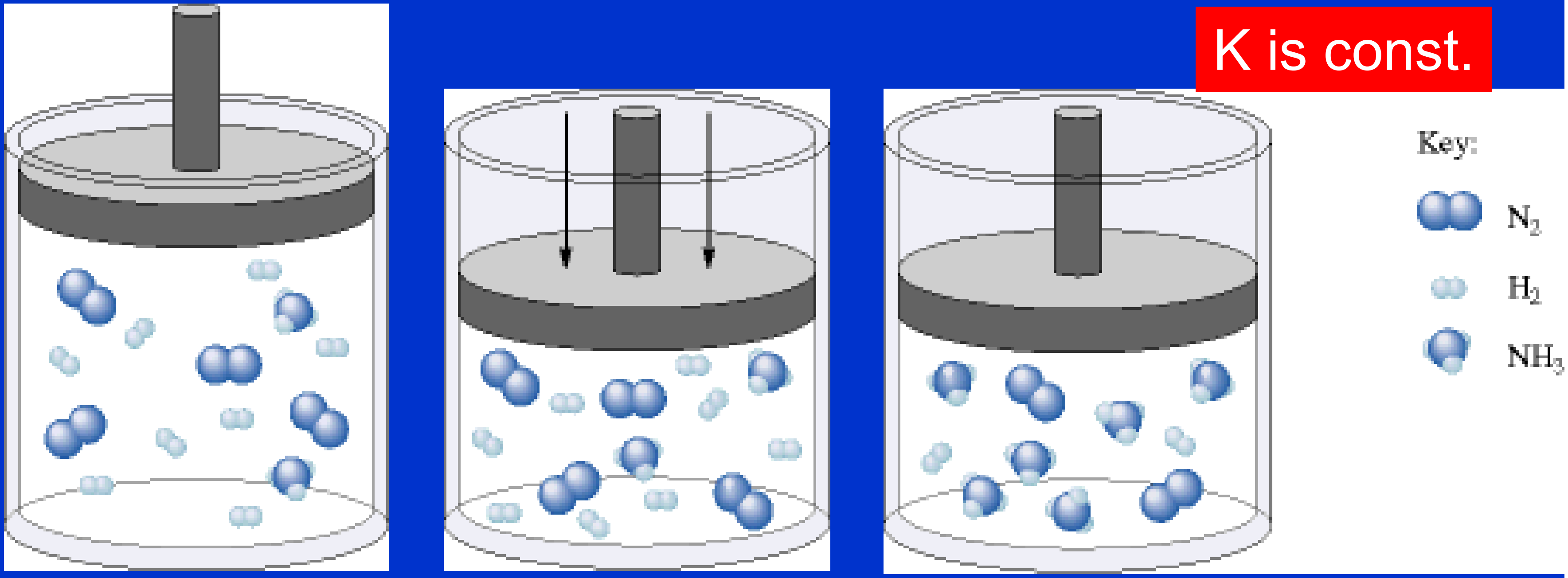
Conditions

20-100 MPa and 400-600 °C



Pressure

K is const.



$$N_2(g) + 3\,H_2(g) \leftrightarrows 2\,NH_3(g)$$

Equilibrium Constant K

$pV = nRT \quad p = (n/V)RT = cRT$

$p = p_1 + p_2 + p_3 + \ldots\ldots$ Partial pressures

$N_2(g) + 3\,H_2(g) \leftrightarrows 2\,NH_3(g)$

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{C_{NH_3}{}^2}{(C_{N_2})(C_{H_2}{}^3)}$$

$$= \frac{\left(\frac{P_{NH_3}}{RT}\right)^2}{\left(\frac{P_{N_2}}{RT}\right)\left(\frac{P_{H_2}}{RT}\right)^3} = \frac{P_{NH_3}{}^2}{(P_{N_2})(P_{H_2}{}^3)} \times \frac{\left(\frac{1}{RT}\right)^2}{\left(\frac{1}{RT}\right)^4}$$

$$= \frac{P_{NH_3}{}^2}{(P_{N_2})(P_{H_2}{}^3)}(RT)^2$$

$$= K_p(RT)^2$$

Equilibrium Constant K

$$jA + kB \leftrightarrows lC + mD$$

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

$$\Delta n = (l + m) - (j + k)$$

$$K_p = \frac{(P_C{}^l)(P_D{}^m)}{(P_A{}^j)(P_B{}^k)} = \frac{(C_C \times RT)^l (C_D \times RT)^m}{(C_A \times RT)^j (C_B \times RT)^k}$$

$$= \frac{(C_C{}^l)(C_D{}^m)}{(C_A{}^j)(C_B{}^k)} \times \frac{(RT)^{l+m}}{(RT)^{j+k}} = K(RT)^{(l+m)-(j+k)}$$

$$= K(RT)^{\Delta n}$$

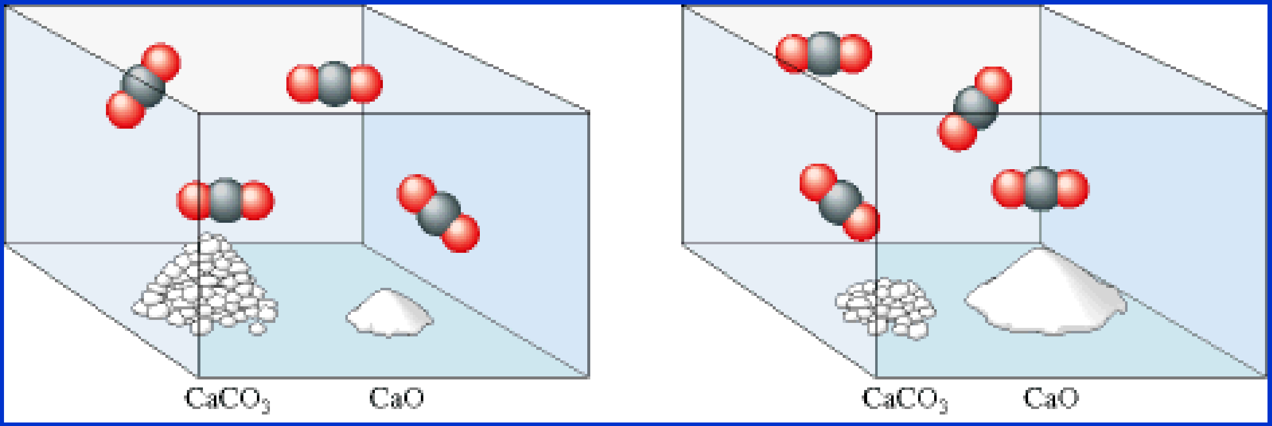
Heterogeneous Equilibria

$CaCO_3(s) \leftrightarrows CaO(s) + CO_2(g)$

$K = [CO_2][CaO] / [CaCO_3] =$ $[CO_2] = p(CO_2)$

Activity (concentration) of pure liquids and solids is constant and does not appear in K.

$[CaO] = [CaCO_3] = \text{const.}$ Addition does not change K



Heterogeneous Equilibria

$2H_2O(l) \leftrightarrows 2H_2(g) + O_2(g)$

$K = [H_2]^2[O_2]$ $K_p = p^2(H_2)\, p(O_2)$

$2H_2O(g) \leftrightarrows 2H_2(g) + O_2(g)$

$K = [H_2]^2[O_2] / [H_2O]^2$ $K_p = p^2(H_2)\, p(O_2) / p^2(H_2O)$

$\Delta G^0 = -RT \ln K$

Temperature

$$\ln K = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

K changes with T

Compare K at T_1 and T_2 (K_1 and K_2)

$$\ln K_2 = -\frac{\Delta H^0}{RT_2} + \frac{\Delta S^0}{R}$$

van’t Hoff equation

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Temperature

cooling →

← heating

$2\,NO_2\,(g) \leftrightarrows N_2O_4\,(g) \quad \Delta H^\circ = -63\ \text{kJ mol}^{-1}$

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Exothermic reactions shift to right

$T_2 < T_1$

on cooling = K incr., $K_2 > K_1$

Heat is a product in exothermic reaction

$2\,NO_2\,(g) \leftrightarrows N_2O_4\,(g) + Q$

Equilibria in Exothermic Reactions

$N_2(g) + 3\,H_2(g) \leftrightarrows 2\,NH_3(g) \qquad \Delta H^\circ = -\,92\ \text{kJ mol}^{-1}$

Yield decreases with increasing T

Incr. T

T, K	K
500	90
600	3
700	0.3
800	0.04

Decr. K and yield

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Temperature

$CaCO_3(s) \leftrightarrows CaO(s) + CO_2(g)$ $\Delta H^\circ = 556$ kJ mol^{-1}

Endothermic reactions shift to right on heating

$T_2 > T_1$

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

K incr, $K_2 > K_1$, $K = p(CO_2)$

Heat is a reactant in endothermic reactions

$CaCO_3(s) + Q \leftrightarrows CaO(s) + CO_2(g)$

Equilibrium Concentrations

$H_2(g) + F_2(g) \leftrightarrows 2HF(g)$

$K = 1.15\ 10^2 = [HF]^2 / [H_2][F_2]$

$[H_2]_0 = 1.00\ M \quad [F_2]_0 = 2.00\ M \quad [HF]_0 = 0$

	$H_2(g)$	$F_2(g)$	$2HF(g)$
Initial	1.00	2.00	0
Change	$-x$	$-x$	$+2x$
Equilibrium	$1.00 - x$	$2.00 - x$	$2x$

$K = 1.15\ 10^2 = [HF]^2 / [H_2][F_2] = (2x)^2 / (1.00 - x)(2.00 - x)$

Equilibrium Concentrations

$x_{1,2} = [-\,b \pm (b^2 - 4ac)^{½}] / 2a$

x_1 = 2.14 mol l^{-1} a x_2 = 0.968 mol l^{-1}

Use
x_2 = 0.968 mol l^{-1}

$[H_2]$ = 1.000 M – 0.968 M = 3.2 10^{-2} M

$[F_2]$ = 2.000 M – 0.968 M = 1.032 M

$[HF]$ = 2 (0.968 M) = 1.936 M