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UNIVERSITY**



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Development of Complex Curricula for Molecular Bionics and Infobionics Programs within a consortial* framework**

Consortium leader

PÁZMÁNY PÉTER CATHOLIC UNIVERSITY

Consortium members

SEMMELWEIS UNIVERSITY, DIALOG CAMPUS PUBLISHER

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**Molekuláris bionika és Infobionika Szakok tananyagának komplex fejlesztése konzorciumi keretben

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WORLD OF MOLECULES

(Molekulák világa)

THERMODYNAMICS

(Termodinamikai alapok)

KRISTÓF IVÁN

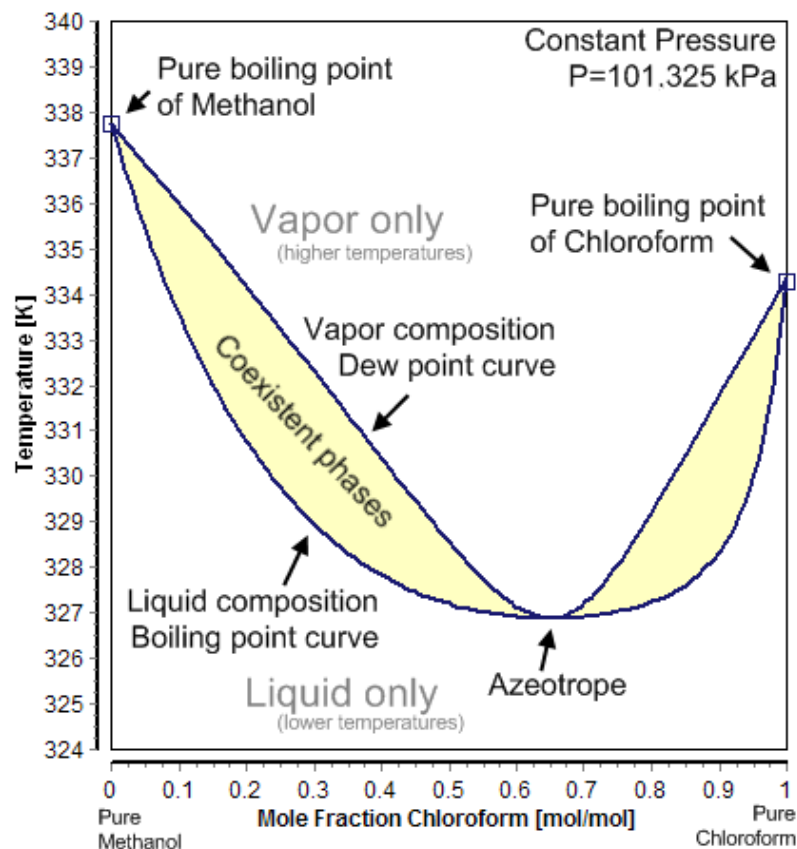


Previously – Solutions, mixtures

1. mixtures
2. miscibility
3. solubility
4. azeotropes, eutectic systems
5. colligative properties
 - lowering of vapor pressure
 - freezing point depression, boiling point elevation
 - osmosis pressure



Previously – Liquid – vapor equilibrium: positive azeotropes

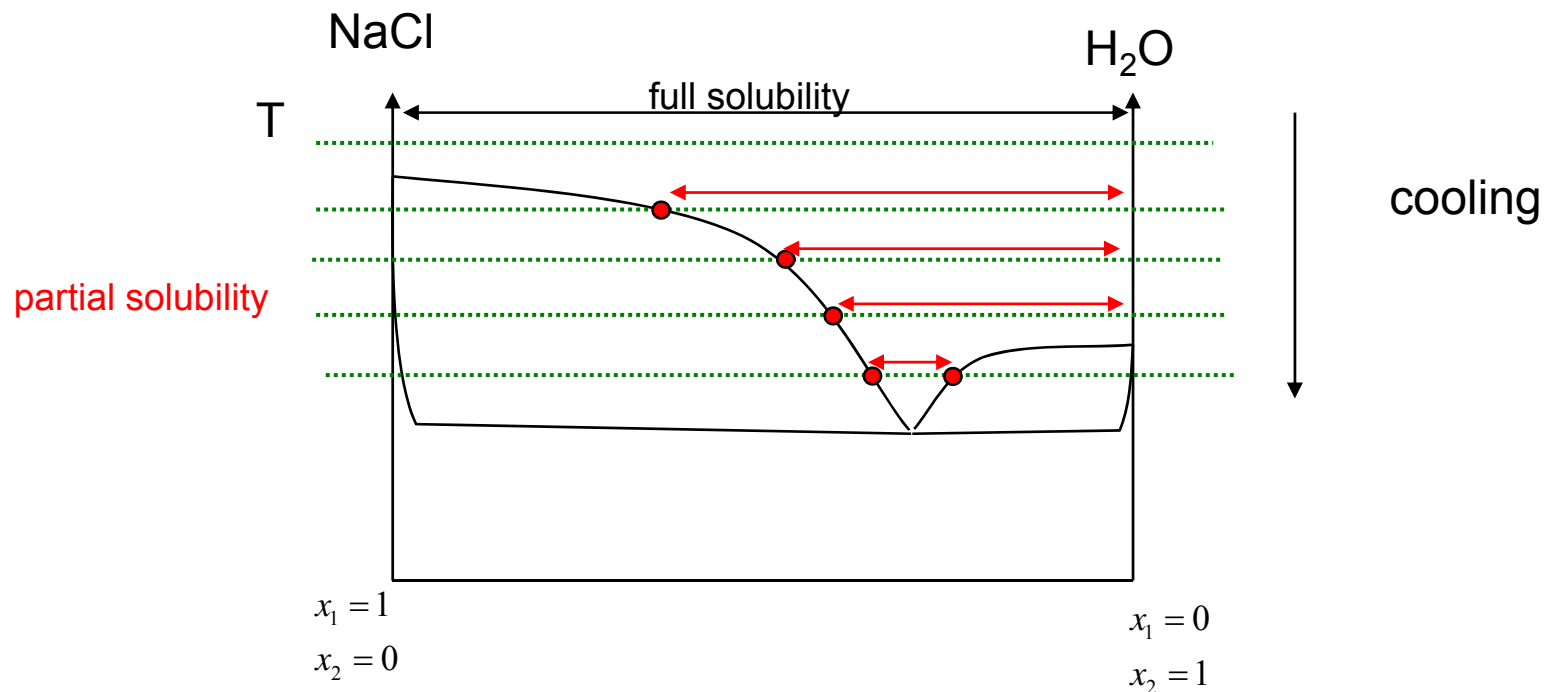


T-x diagram of a minimum azeotrope chloroform and methanol

http://en.wikipedia.org/wiki/File:Positive_Azeotrope.png

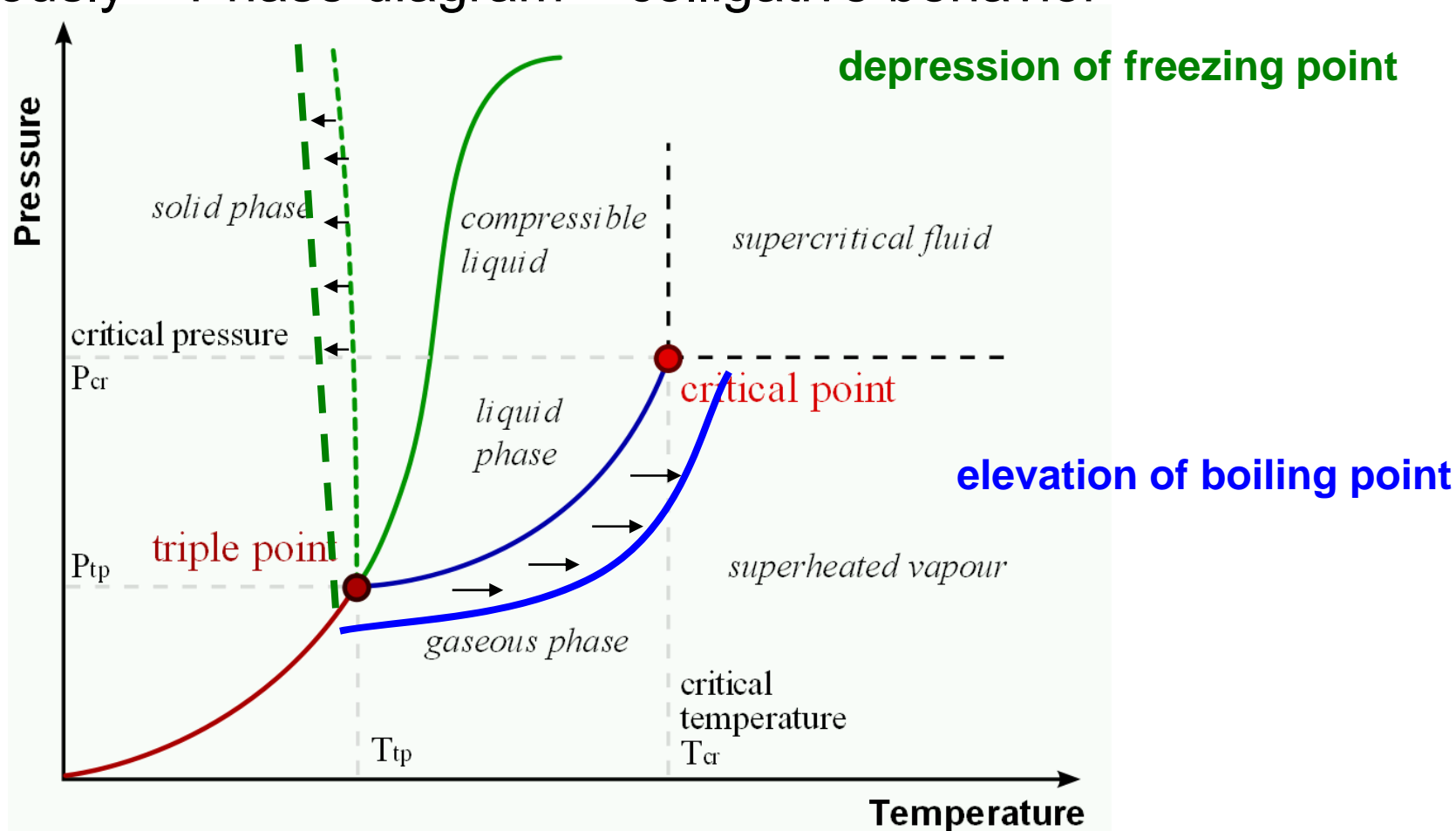
Previously – Two component systems - Liquid – solid equilibrium

- eutectic systems
- the change of solubility at different temperatures
- solubility limit (saturated solutions...)





Previously – Phase diagram – colligative behavior



<http://en.wikipedia.org/wiki/File:Phase-diag2.svg>





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4. Heat
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Intensive and extensive quantities

Intensive quantities

- does not depend on the measure (size, amount, mass) of the system – size invariant
e.g. temperature, pressure, density, surface tension, chemical potential, molar volume, ...

Extensive quantities

- depends on the amount/size of the system
e.g. mass, volume, length, resistance, entropy, enthalpy, energy





Intensive and extensive quantities

the quotient of two extensives gives an intensive quantity

e.g.
$$\frac{\text{mass (extensive)}}{\text{volume (extensive)}} = \textit{density} \text{ (intensive)}$$

connecting two separate thermodynamic systems with different measures will result in the two systems changing towards a common equilibrium

during this

the **extensives** are added

the **intensives equilibrate** between the two systems





Thermodynamics

- originally the science of heat exchange and transfer
- versatile application areas
- in chemistry
 - energy relations of chemical reactions
 - description of spontaneous reactions
 - characterization of equilibrium processes
 - energy associated with phase changes
 - energy of solution processes





Thermodynamics

Laws of thermodynamics

0. If systems A and B are in equilibrium, and A and C also, then B and C are also in equilibrium

- equilibrium: the intensive state variables of interactions are equalized (e.g. pressure, temperature)
- the system does not leave equilibrium state proprio motu



Thermodynamics

Laws of thermodynamics

1. conservation of energy

$$\Delta U = W + Q$$

the energy (ΔU) of a closed system at rest can only be changed by work (W) or heat (Q)

- at constant pressure $\Delta U = -p\Delta V + Q_p$
- if heated the internal energy increases and/or work is done on the systems $Q_p = \Delta U + p\Delta V$
- energy cannot be created from nothing
- perpetuum mobile of the first kind is impossible

Thermodynamics

Laws of thermodynamics

2. entropy

when 2 thermodynamic systems are connected their entropy will increase until equilibrium is reached

- in spontaneous processes (where the system changes until equilibrium) the entropy is always increasing

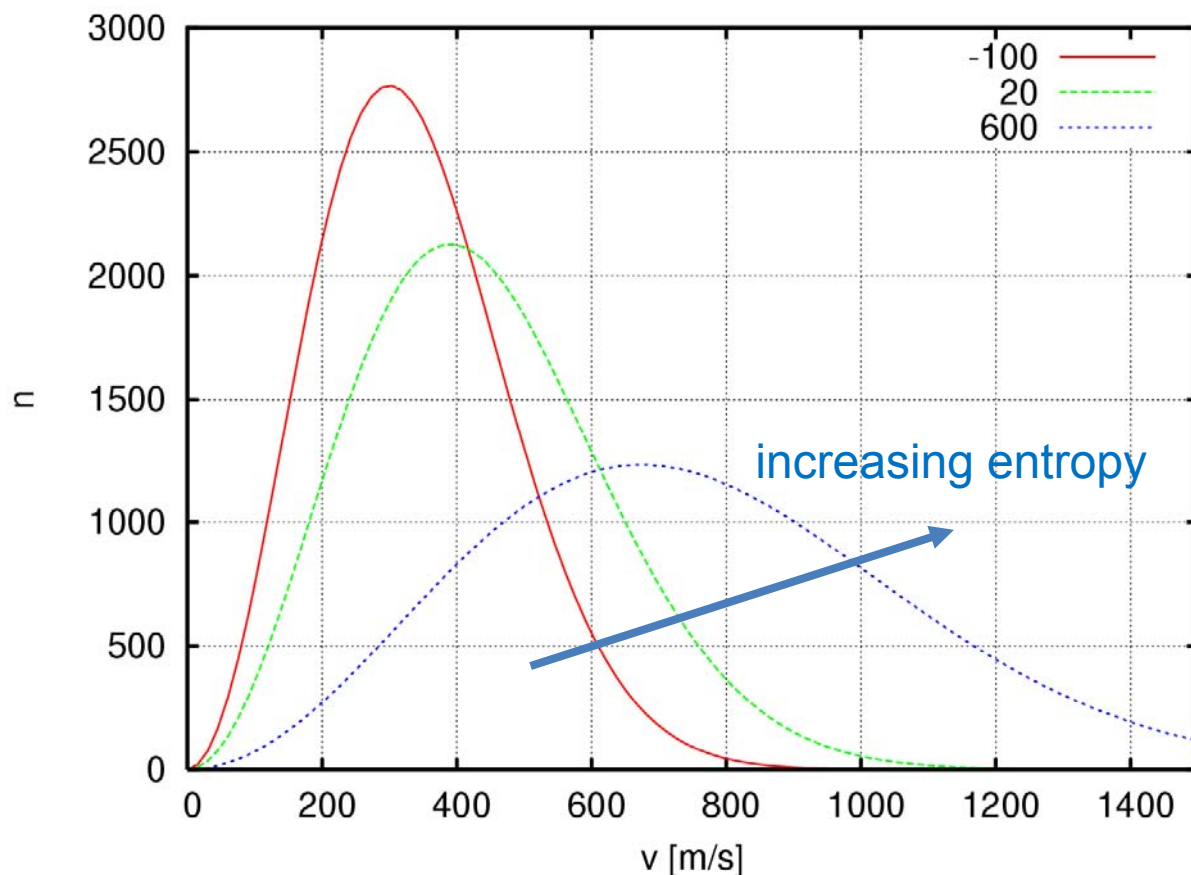
- entropy is the measure of the disorder (randomness) of a system

$$S = k_B \cdot \ln w$$

the thermodynamic probability of microstates (w)



Maxwell-Boltzmann distribution of molecule speeds



speed distribution of
of 1 million gas
molecules
at -100, 20 and
600 degrees °C

http://it.wikipedia.org/wiki/File:Maxwell-Boltzmann_distribution_1.png





Thermodynamics

Laws of thermodynamics

3. absolute zero temperature

at the temperature of absolute 0 (Kelvin) the entropy of a flawless crystal is zero

- absolute zero temperature can never be reached
- no flawless crystal exists
- if the system is asymptotically approaching zero temperature all processes halt and the entropy of the system approaches a minimum (asymptotically)

$$\lim_{T \rightarrow 0} \Delta S = 0$$





Enthalpy

Enthalpy – heat of reaction

the amount of heat which was released or absorbed during the chemical reaction

$$\Delta H = \Delta U + \Delta(pV)$$

$$\Delta H = Q_p = \Delta U + p\Delta V \quad \text{at constant pressure}$$

$$\Delta H < 0 \quad \text{Exotherm reactions}$$

$$\Delta H > 0 \quad \text{Endotherm reactions}$$

$$\Delta U = -p\Delta V + T\Delta S, \quad \Delta U + p\Delta V = \Delta H = T\Delta S$$





Enthalpy

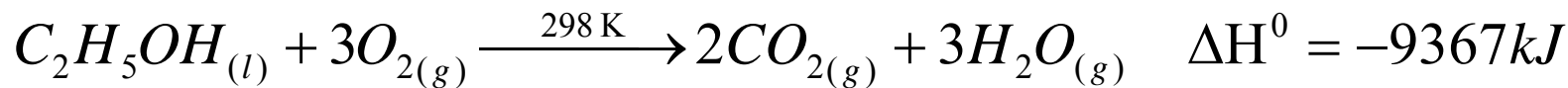
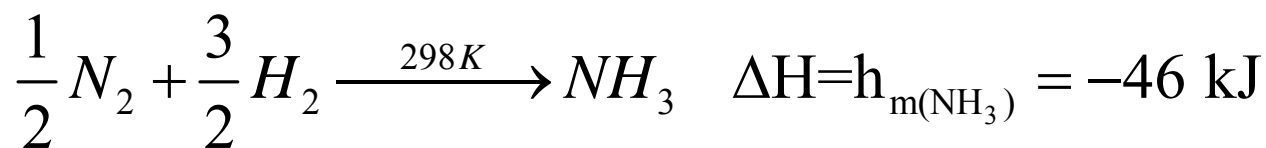
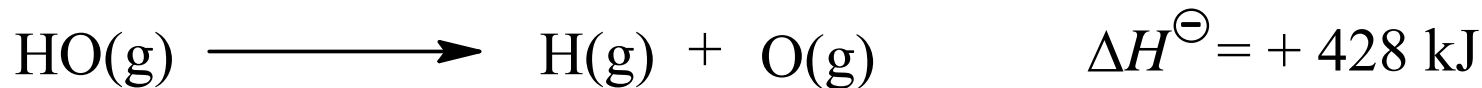
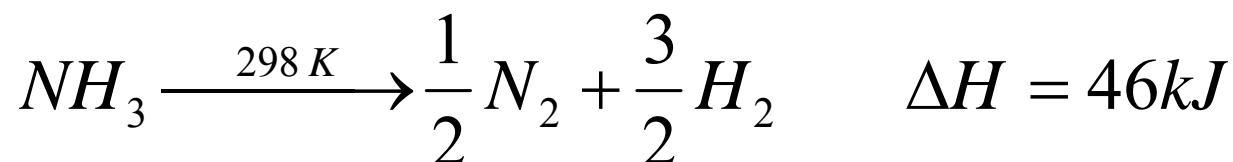
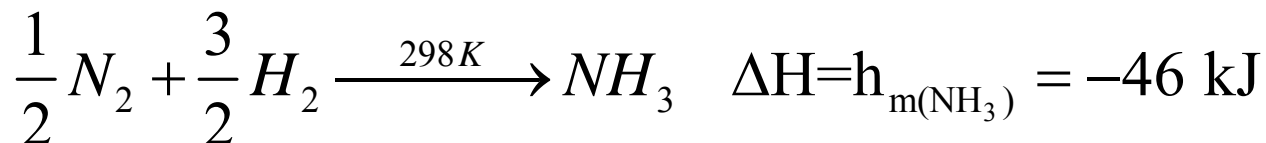
types of enthalpy

- heat of reaction (in general)
- heat of formation (from elementary forms)
- heat of bond formation
- heat of combustion (in pure oxygen)
- heat of atomization (dissociate into its elementary building atoms)
- heat of hydration (dissolution in liquid water)
- heat of fusion (solid to liquid state)
- heat of vaporization (liquid to vapor phase)
- heat of sublimation (solid to vapor phase)





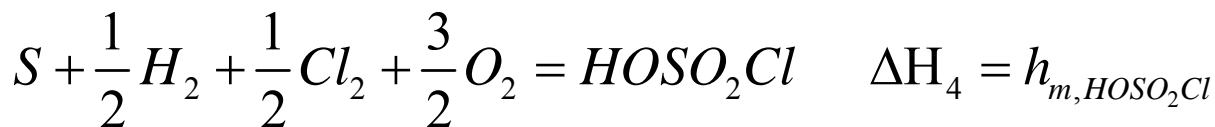
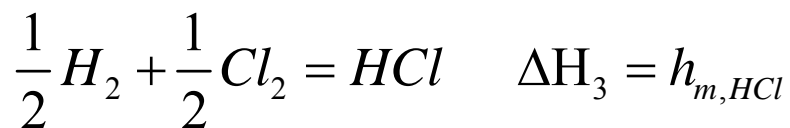
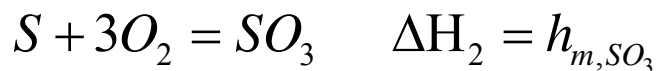
Enthalpy - examples



Enthalpy

The heat of reaction can be calculated using the molar heats (h_m) of formation of the reactants and the products

$$\Delta H = \underbrace{\sum_i h_{m,i} \cdot n_i}_{\text{products}} - \underbrace{\sum_j h_{m,j} \cdot n_j}_{\text{reactants}}$$



$$\Delta H_1 = \Delta H_4 - (\Delta H_2 + \Delta H_3) = h_{m,HOSO_2Cl} - (h_{m,SO_3} + h_{m,HCl})$$

Gibbs free energy



what determines the direction of spontaneous processes? : Gibbs free energy (ΔG)

$$\Delta U = W + Q$$

$$\Delta U = -p\Delta V + Q_p$$

$$\Delta U = -p\Delta V + T\Delta S + \mu\Delta n$$

non-mechanical work
(here: transport of chemical species)

$$\Delta U + p\Delta V = \Delta H = T\Delta S + \mu\Delta n$$

$$\Delta G = \Delta H - T\Delta S = \mu\Delta n$$

$$\Delta G = \mu\Delta n$$

Gibbs free energy

Gibbs free energy of formation (Δg): the non-mechanical work associated with the formation of a compound from its elements

- the chemical potential can be described as:

$$\mu_i = \mu_i^0 + RT \ln c_i \quad \mu_i = \mu_i^0 + RT \ln p_i$$

$$\mu_i = \mu_i^0 + RT \ln x_i$$

- the Gibbs free energy of a reaction (similarly to enthalpy)

$$\Delta G = \underbrace{\sum_i g_{m,i} \cdot n_i}_{\text{products}} - \underbrace{\sum_j g_{m,j} \cdot n_j}_{\text{reactants}}$$

Gibbs free energy

expressing ΔG for the following reaction

$$aA + bB \longrightarrow cC + dD$$
$$\Delta G = \Delta G^0 + RT \ln \left(\frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} \right) \quad \text{using} \quad \Delta G = nRT \ln \frac{p_2}{p_1}$$

in equilibrium we can write

$$\Delta G = 0$$

$$\Delta G^0 = -RT \ln K_p \quad \text{where} \quad K_p = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$$

in case we have a reaction in the liquid phase:

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

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

$$\Delta G^0 = -2.3RT \log K$$



The relationship between ΔG° and K at 25 °C

ΔG° [kcal/mol]	K	product conversion ratio [%]
- 0.1	1.2	54.5
- 0.5	2.4	69.7
- 1	5.4	84.4
- 2	29.3	96.7
- 5	4631	99.98
- 10	2.1×10^7	99.999996





Next – Electrochemistry

1. Electrolytes
2. Electrochemistry
3. Concentration cells
4. Galvanic cell
5. Electromotive force
6. Standard electrode potentials
7. Redox reactions
8. Electrolysis

