Basics of chemical thermodynamics and kinetics

Textbook for students of Materials Engineering

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This textbook was prepared for students of the 2nd year of Materials Engineering at Faculty of Mechanical Engineering, Brno University of Technology. It should help the students to prepare for the exam of Basics of chemical thermodynamics and kinetics.

Brno, 2005, Dr. Karel Maca

CONTENT:

1. BASIC CONCEPTS OF CHEMICAL THERMODYNAMICS

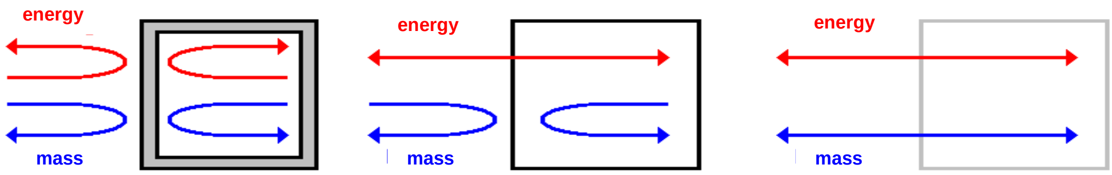
THERMODYNAMICS is a science explaining mutual conversions of various types of energies (e.g. heat and mechanical work), directions of spontaneous physical and chemical processes (changes of systems' states), and equilibriums.

Thermodynamics

- investigates macroscopic systems' properties (p, V, T,…)
- enables e.g. to determine thermodynamic probability of a given chemical reaction (and their condition and yield)
- enables e.g. to determine thermal balance of physical and chemical processes
- does not show the speed of reaction and changes

Thermodynamic system
is a part of space, which is separated out of its surrounding by real or virtual boundaries

Classification of thermodynamic systems according to relation to their surrounding



isolated system closed system open system

Classification of thermodynamic systems according to their chemical composition
Composition of the system: the number of a chemically distinct constituent of a system (compounds) = the number of components
*Single-component system***:** only one component in the system
*Multi-component system***:** more than one component in the system

Classification of thermodynamic systems according to their phase composition
Homogenous system (= phase): intensive properties are constant (or continuously changing) in the whole system
Heterogeneous system: compiled from two or more homogenous parts (phases), the intensive properties are changed discontinuously at the phases' boundaries

State of the system
is given by the sum of its state properties

<u>Thermodynamic variables (state variables, state parameters,</u> e.g. p, T, V, U, n,…) - describe the momentary condition of a thermodynamic system. Regardless of the path by which a system goes from one state to another — i.e., the sequence of intermediate states — the total change in any state variable will be the same.

Extensive property (m, V, U, n…) of a system does depend on the system size or the amount of material in the system. They are additive.

Intensive property (p, T, ρ, V_m…) of a system does not depend on the system size or the amount of material in the system. Differences in intensive properties are driven forces of thermodynamics processes leading to their equalizing ant to thermodynamics equiloibrium.

The number of state variables which are necessary for complete description of the state of the system is increasing with increasing number of compounds and phases. It is e.g. necessary two state variables (except quantity) for the full description of the simplest system (one component, one phase).

Thermodynamic process and equilibrium

Thermodynamic process takes place when the state of the system is changing
Thermodynamic equilibrium occurs when composition and state variables are constant

Reversible process – is a process that can be "reversed" by means of infinitesimal changes in some property of the system without loss or dissipation of energy. Due to these infinitesimal changes, the system is in thermodynamic equilibrium throughout the entire process. So that the process can be defined by a mathematical function.
Irreversible process – any other than reversible transit from one to another system state - finite changes are made; therefore the system is not at equilibrium throughout the process

2. ZEROTH, FIRST, SECOND (AND THIRST) LAWS OF THERMODYNAMICS

are basic axioms of thermodynamics postulated on the basis of long-term experiences and observations

Zeroth thermodynamics law

If two thermodynamic systems are separately in thermal equilibrium with a third, they are also in thermal equilibrium with each other.

Zeroth law explains the concept of temperature. It implies that thermal equilibrium is an equivalence relation on the set of thermodynamic systems. This law is tacitly assumed in every measurement of temperature. Thus, if we want to know if two bodies are at the same temperature, it is not necessary to bring them into contact and to watch whether their observable properties change with time – we can use a standard: thermometer.

Temperature measurement

utilizes properties which are continuously and reproducibly changed with the temperature:
- length (or volume) changes (β=3 α)
- electric resistivity
- thermoelectric voltage
- …

Celsius scale
0°C – melting temp. of ice at normal pressure (101 325 Pa)
100°C – boiling temperature of water at normal pressure

Kelvin scale
The temperature of water triple point is 273,16 K
The temperature 0°C = 273,15 K

T[K] = t [°C] + 273,15

Types of energies in systems and processes between them

Internal energy (U) **–** is the total "internal" energy of the system. It contains the kinetic energy due to the motion of particles (translational, rotational, vibrational) and the potential energy associated with the vibrational and electric energy of atoms within molecules or crystals. It includes the energy in all of the chemical bonds, and the energy of the free, conduction electrons in metals

Heat (Q) **–** is the process of energy transfer from one system (at higher temperature) to another system (at lower temperature) due to thermal contact (in any other way than due to work). It is positive when energy is transferred into the system and opposite.

Work (W) **–** performed by a system is the quantity of energy transferred by the system to another due to changes in the external parameters of the system (most frequently volume). It is positive when the volume is increasing. Work performed by a system:

$$dW = F \cdot ds = p \cdot S \cdot ds = p \cdot dV$$
$$W = \int dW = \int p dV$$

Example: How you can demonstrate in p-V diagram that work is not a state variable?

First thermodynamic law

It expresses the law of energy conservation in thermodynamic systems.

$$\boxed{\mathbf{dU = \delta Q - \delta W = \delta Q - pdV}}$$

The change in the internal energy of a closed thermodynamic system is equal to the sum of the amount of heat energy supplied to or removed from the system and the work done on or by the system.

Second thermodynamic law

It extends 1st TL by means of assignation of direction of thermodynamic processes, i.e., it determines which processes can proceed at a given temperature, pressure and concentration spontaneously, without external work consumption.

The groung of 2nd TL is the difference between heat and work: work is ordered (macroscopic) form of energy transfer, heat is disordered (microscopic) way of energy transfer. Therefore change of work into heat is not bonded by any conditions, opposite process is limited by 2nd TL.

There are many equivalent formulations of the 2nd TL:
- Heat cannot spontaneously flow from a colder location to a hotter area - work is required to achieve this (Clausius)
- It is impossible to convert heat completely into work in a cyclic process (Kelvin)
- The temperature of 0K cannot be reached
- Effectivity of the Carnot cycle is always less than 1

$$\eta = \frac{Q_2 - Q_1}{Q_2} = \frac{T_2 - T_1}{T_2} < 1$$

- Heat has an integration factor $\frac{1}{T}$, so $\oint \frac{1}{T}\delta Q = 0$ => definition of entropy as a state variable:

$$dS = \frac{\delta Q}{T} \quad \text{(Clausius)}$$

- In closed systems entropy either grow (nonreversible processes) or stay constant (reversible processes)

Entropy is a bridge between thermodynamics and statistics::

There are two equivalent ways how to define changes of entropy in the system:

1) macroscopically: $dS = \frac{\delta Q}{T}$
2) microscopically – calculation of all possibilities how can be atoms or molecules assembled in the system

<u>Third thermodynamic law</u>

S = 0 J/K at a temperature of T =0 K => entropy is only one thermodynamic variable which can be calculated absolutely

3. THERMODYNAMIC RELATIONS AND VARIABLES

Thermodynamic (TDM) variables of closed systemsémů

<u>1st TL</u>: $dU = \delta Q - \delta W = \delta Q - pdV$ <u>2nd TL</u>: $\delta Q = TdS$

<u>1st + 2nd TL</u>: $\mathbf{dU = TdS - pdV,}$ $\mathbf{U = U(S,V)}$

Internal energy U is the TDM variable with external parameters S and V. External parameters are such physical properties which we are able to change or keep constant.

Transit to other TDM variables with different external parameters (Legendre transformation):

$dU = TdS - pdV - d(pV) + pdV + Vdp$

$d(U+pV) = \mathbf{dH = TdS + Vdp,}$ $\mathbf{H = H(S,p),}$ $\mathbf{H = U+pV}$

$dH = TdS + Vdp + d(TS) - TdS - SdT$

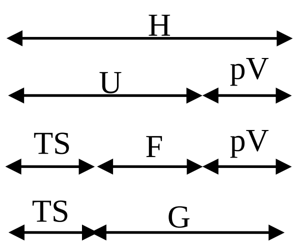
$d(H - TS) = \mathbf{dG = - SdT + Vdp,}$ $\mathbf{G = G(T,p),}$ $\boxed{\mathbf{G = H-TS}}$

$dU = TdS - pdV + d(TS) - TdS - SdT$

$d(U-TS) = \mathbf{dF = -SdT - pdV,}$ $\mathbf{F = F(T,V),}$ $\mathbf{F = U-TS}$

Example: how we can derive dF from dG?

Scheme of relations among various TDM variables:



H (S,p)…enthalpy

U (S,V)…internal energy

F (T,V)…free energy (Helmholtz energy)

G (T,p)…free enthalpy (Gibbs energy)

<u>TERMOCHEMISTRY</u>

answers two basic questions:

1. How is the temperature of a system changed by adding of some amount of heat? (heat capatities)
2. Which thermal effect do accompany given chemical reaction or change of the phase state, or creation (dilution) of solutions, …? (heat of reaction, phase transformation,…)

Heat capacities

Heat capacity is the measure of the heat energy required to increase the temperature of an object by a certain temperature interval (e.g. by 1°C)

Specific heat capacity: $c = \Delta Q/(m\cdot\Delta T)$ [J/(kg·K)]
Molar heat capacity: $C = \Delta Q/(n\cdot\Delta T)$ [J/(mol·K)]

mean heat capacity: average value in a given temperature interval $\Delta T = T_2 - T_1$
true heat capacity: value valid exactly at a given temperature ($\Delta T \to 0$)

Example: relation between c and C? $n = m/M \Rightarrow C = c\cdot M$ - watch units, M is in g/mol !

Heat capacities at constant volume and pressure

$dU = TdS - pdV = \delta Q - pdV$, $V = \text{const.} \Rightarrow dU = C_V dT$
$dH = TdS + Vdp = \delta Q + Vdp$, $p = \text{const.} \Rightarrow$ $\mathbf{dH = C_p dT}$

Many physical-chemical processes proceed at constant pressure, therefore enthalpy often means heat (released or consumed during the process)

It is valid for ideal gas: $C_p - C_V = R$ - derivation

Dulong – Petit rule: $C_{\text{solid elements}}$ = 25-26 J/mol·K
Example: A metal has c=0,0323cal/g·K. Which metal is it?

Neuman-Kopp rule: $C_{A_xB_y} = x\cdot C_A + y\cdot C_B$
Used e.g. in metallurgy and foundry engineering for estimation of heat capacities of slags

Temperature capacities of heat capacities
The temperature has a considerable effect on heat capacity. It is measured by calorimetric or spectral experiments.

$$\Delta Q_{mol} = \int_{T_1}^{T_2} C_p(T)\,dT$$

Most frequent expression of temperature dependence of heat capacity:
$C_p(T) = a + b\cdot T$
$C_p(T) = a + b\cdot T + c\cdot T^2 + c\cdot T^3 + \ldots$
$C_p(T) = a + b\cdot T + c\cdot T^{-2}$

HEAT OF REACTION (STANDARD ENTHALPY CHANGE OF REACTION)

Heat of reaction is the amount of heat which system changes with its surrounding during the reaction

Most of chemical reactions proceed at a constant pressure, therefore heat of reaction is often characterized by the change of enthalpy

$$dH = TdS + Vdp, \quad p = const. \Rightarrow \quad dH = \delta Q$$

$\Delta H > 0$ => enthalpy of products is higher than input reactants
endothermic reaction (process)
$\Delta H < 0$ => enthalpy of products is lower than input reactants
exothermic reaction (process)

Absolute values of enthalpy (as well as internal energy) of matters are not known, therefore enthalpy is expressed in relation to enthalpy of the matter in exactly defined state - **standard state**

Standard state of gases: ideal gas at p = 101 325 Pa and given temperature (usually 298,15 K)
Standard state of liquids: liquid at p = 101 325 Pa and given temperature
Standard state of solids: most stable solid modification at p = 101 325 Pa given temperature

Enthalpy of matter A at a temperature of T: $(\Delta H^0{}_T)_A$

Question: How is enthalpy of elements at standard state?

Standard heat (enthalpy) of formation of a compound is the change of enthalpy that accompanies the formation of 1 mole of a substance in its standard state from its constituent elements in their standard states (the most stable form of the element at 101 325 Pa of pressure and the specified temperature, usually 298.15 K or 25°C). Standard heats (enthalpies) of formation are given in thermodynamic tables.

Question: How is enthalpy of formation of elements?

Calculation of standard heat of formation of chemical reaction

$$aA + bB + \ldots \Leftrightarrow rR + sS + \ldots$$

$$(\Delta H^0_{T_0})_r = r \cdot (\Delta H^0_{T_0})_{form.,R} + s \cdot (\Delta H^0_{T_0})_{form.,S} - a \cdot (\Delta H^0_{T_0})_{form.,A} - b \cdot (\Delta H^0_{T_0})_{form.,B}$$

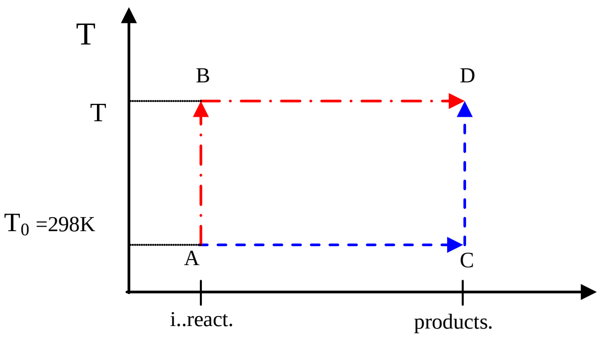
$$\boxed{\left(\Delta H^0_{T_0}\right)_r = \sum_{j=prod.} n_j \left(\Delta H^0_{T_0}\right)_{form.,j} - \sum_{i=i.reac.} n_i \left(\Delta H^0_{T_0}\right)_{form.,i}}$$

Some thermochemistry laws:

1st TChL (Lavoiser and Laplace's law, 1780): The energy change accompanying any transformation is equal and opposite to energy change accompanying the reverse process.

2nd TChL (Hess's law, 1840): The energy change accompanying any transformation is the same whether the process occurs in one step or many.

Temperature dependence of heat of reaction – Kirchoff's equation



We want to calculate reaction heat at temp. T (B→D) Due to 2nd TChL, it is the same case when system goes from state A to state D through point C (reaction occurs at temperature T_0 and then the products are heated), or through B (firstly input reactants are heated and then reaction occurs)

$$\left(\Delta H^0_{T_0}\right)_r + \sum_{j=prod.} n_j \int_{T_0}^{T_1} C_{p,j} dT = \left(\Delta H^0_{T_1}\right)_r + \sum_{i=i.react.} n_i \int_{T_0}^{T_1} C_{p,i} dT$$

Kirchoff's equation – integral form

$$\boxed{\left(\Delta H^0_{T_1}\right)_r = \left(\Delta H^0_{T_0}\right)_r + \int_{T_0}^{T_1} \Delta C_{p,j} dT \text{ , where } \left(\Delta H^0_{T_0}\right)_r = \sum_{j=prod.} \left(\Delta H^0_{T_0}\right)_{form.,j} - \sum_{i=i.react.} \left(\Delta H^0_{T_0}\right)_{form.,i} \quad \Delta C_p = \sum_{j=prod.} n_j C_{p,j} - \sum_{i=i.react.} n_i C_{p,i}}$$

For most frequent type of temperature dependance of heat capacity $C_p = a + bT + cT^{-2}$:

$$\boxed{\left(\Delta H^0_{T_1}\right)_r = \left(\Delta H^0_{T_0}\right)_r + \Delta a \cdot (T_1 - T_0) + \frac{1}{2} \Delta b \cdot (T_1^2 - T_0^2) - \Delta c \cdot \left(\frac{1}{T_1} - \frac{1}{T_0}\right)} \qquad (1)$$

Example:

Calculate thermal balance of reaction $MnO_2(s) + 2H_2(g) \leftrightarrow Mn(s) + 2H_2O(g)$ at 1000K.

Compound	$(\Delta H^0_{298})_{form.}$ [kcal / mol]	$C = a + bT + cT^{-2}$ a [cal/K·mol]	b [cal/K^2·mol]	c [cal·K/mol]	tepl. rozsah
$MnO_2(s)$	-124.3	16.60	$2.44 \cdot 10^{-3}$	$-3.88 \cdot 10^5$	298 – 1000 K
$H_2(g)$		6.52	$0.78 \cdot 10^{-3}$	$0.12 \cdot 10^5$	298 – 3000 K
$Mn(s)$		6.03	$3.56 \cdot 10^{-3}$	$-0.44 \cdot 10^5$	298 – 1410 K
$H_2O(g)$	-57.795	7.17	$2.56 \cdot 10^{-3}$	$0.08 \cdot 10^5$	298 – 2500 K

Solution:

$(\Delta H^0_{298})_r$ = -2*57.795 – (–124.3) = +8.71 kcal/mol$_{Mn}$

Δa = 2*7.17 + 6.03 – (2*6.52 + 16.60) = –9.27 cal/K·mol$_{Mn}$
Δb = [2*1.56 + 3.56 – (2*0.78 + 2.44)] $\cdot 10^{-3}$ = $4.68 \cdot 10^{-3}$ cal/K^2·mol$_{Mn}$
Δc = [2*0.08 – 0.44 – (2*0.12 – 3.88)] $\cdot 10^5$ = $3.36 \cdot 10^5$ cal·K/mol$_{Mn}$

$(\Delta H^0{}_T)_r = (\Delta H^0{}_{298})_r + \Delta a*(T\text{-}298) + ½\Delta b*(T^2\text{-}298^2) - \Delta c*(\frac{1}{T} - \frac{1}{298})$

$(\Delta H^0{}_{1000})_r = 8710 – 9.27*702 + 2.34 \cdot 10^{-3}*(1000 \cdot 10^3 – 88.8 \cdot 10^3) – 336 \cdot 10^3* (1 \cdot 10^{-3} – 3.36 \cdot 10^{-3})$

$= 8710 – 6508 + 2132 + 793 = 5\,127$

$\underline{(\Delta H^0{}_{1000})_r = 5\,127 \text{ cal/mol}_{Mn}}$

Diferential form of Kirchoff's equation:

$\boxed{d(\Delta H^0{}_T) = \Delta C_p dT} = (\Delta a + \Delta bT + \Delta cT^{-2})dT$

after general integration $\boxed{(\Delta H^0{}_T)_r = \Delta a*T + ½\Delta b*T^2 - \Delta c*\frac{1}{T} + I_H}$

(2)

Solution of former example using equation (2)

Calculation of integral constant is performed usually for T = 298K.

$8710 = -9.27*298 + 2.34 \cdot 10^{-3}*298^2 – 3.36 \cdot 10^5/298 + I_H$

$I_H = 8710 + 2762 – 208 + 1128 = 12392$

$(\Delta H^0{}_T)_r = -9.27*T + 2.34 \cdot 10^{-3}*T^2 – 3.36 \cdot 10^5*\frac{1}{T} + 12392$

$(\Delta H^0{}_{1000})_r = -9270 + 2340 – 336 + 12392 = 5126$

$\underline{(\Delta H^0{}_{1000})_r = 5\,126 \text{ cal/mol}_{Mn}}$

4. EQUILIBRIUM IN THERMODYNAMIC SYSTEMS

TEMPERATURE DEPENDENCE OF ENTROPY

2^{nd} TL: $\delta Q = TdS$ => $dS = \frac{\delta Q}{T}$

p = const. => $dS = \frac{C_p dT}{T}$

For chemical reaction with compounds having temperature dependence of heat capacity

$\underline{C_p = a + bT + cT^{-2}}$

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} \left(\frac{\Delta a + \Delta bT + \Delta cT^{-2}}{T} \right) dT$$

$$\left(\Delta S^0_{T_1}\right)_r = \left(\Delta S^0_{T_0}\right)_r + \Delta a \cdot \ln\frac{T_1}{T_0} + \Delta b \cdot (T - T_0) - \frac{1}{2}\Delta c \cdot \left(\frac{1}{T^2} - \frac{1}{T_0^2}\right) \qquad (3)$$

Change of Gibbs energy during spontaneous processes

2^{nd} TL: TdS ≥δQ => δQ – TdS ≤ 0

dG = dH – d(TS) = dU + d(pV) – TdS – SdT = δQ – pdV + pdV + Vdp – TdS – SdT

for T, p =const.: dG = δQ – TdS ≤ 0

dG ≤ 0

TEMPERATURE DEPENDENCE OF GIBBS REACTION ENERGY

1. By calculation from enthalpy and entropy values

$$\boxed{\left(\Delta G^0_{T_1}\right)_r = \left(\Delta H^0_T\right)_r - T\left(\Delta S^0_T\right)_r} \qquad (4)$$

and then using equations (1) and (3)

2. General dependence $\left(\Delta G^0_{T_1}\right)_r = f(T)$

Comparing following relations:

dG = - S dT + V dp

$dG = \left(\frac{\delta G}{\delta T}\right)_p dT + \left(\frac{\delta G}{\delta p}\right)_T dp$ (this is valid for all total diferentials)

we get -S = $\left(\frac{\delta G}{\delta T}\right)_p$

$$\left(\Delta G^0_{T_1}\right)_r = \left(\Delta H^0_T\right)_r - T\left(\Delta S^0_T\right)_r = \left(\Delta H^0_T\right)_r + T\left(\frac{\delta\left(\Delta G^0_T\right)}{\delta T}\right)_p$$

$\Delta H = \Delta G - T\frac{\delta\Delta G}{\delta T}$ using following formula $\frac{\delta\left(\frac{\Delta G}{T}\right)}{\delta T} = \frac{\frac{\delta\Delta G}{\delta T}T - \Delta G}{T^2}$

$\Delta H = -T^2\frac{\delta\left(\frac{\Delta G}{T}\right)}{\delta T}$ => $\delta\left(\frac{\Delta G}{T}\right) = -\frac{1}{T^2}\Delta H\delta T$

For most frequent type of temperature dependance of heat capacity $C_p = a + bT + cT^{-2}$ a and using (2)

$$\int \delta\left(\frac{\Delta G}{T}\right) = \int -\frac{\Delta aT + 0.5\Delta bT^2 - \Delta c/T + I_H}{T^2}\delta T$$

$$\boxed{(\Delta G^0_T)_r = -\Delta a \cdot T \cdot \ln T - ½\Delta b \cdot T^2 - ½\Delta c/T + I_H + I_G \cdot T \quad (5)}$$

Integral constant I_H is calculated from (2) by establishing heats of formation and T = 298K, integral constant I_G is calculated from (5), when

$(\Delta G^0_{298})_r = (\Delta H^0_{298})_r – 298 \cdot (\Delta S^0_{298})_r$

Example:
Calculate temperature dependence of Gibbs free energy and its value at T=1000K $(\Delta G^0_{1000})_r$ of reaction $MnO_2(s) + 2H_2(g) \leftrightarrow Mn(s) + 2H_2O(g)$

Compound	$(\Delta H^0_{298})_{form}$ [kcal/mol]	S^0_{298} [cal/mol·K]	$C = a + bT + cT^{-2}$ a [cal/K·mol]	b [cal/K²·mol]	c [cal·K/mol]	tepl. rozsah
MnO_2(s)	-124.3	12.7	16.60	$2.44 \cdot 10^{-3}$	$-3.88 \cdot 10^5$	298– 1000 K
H_2(g)		31.21	6.52	$0.78 \cdot 10^{-3}$	$0.12 \cdot 10^5$	298– 3000 K
Mn(s)		7.65	6.03	$3.56 \cdot 10^{-3}$	$-0.44 \cdot 10^5$	298– 1410 K
H_2O(g)	-57.795	45.11	7.17	$2.56 \cdot 10^{-3}$	$0.08 \cdot 10^5$	298– 2500 K

Solution:

$\mathbf{(\Delta H^0_{298})_r}$ = -2*57.795 – (–124.3) = **+8.71 kcal/mol$_{\mathbf{Mn}}$**
$\mathbf{(\Delta S^0_{298})_r}$ = 2*45.11 + 7.65 – (2*31.21+12.7) = **22.75 cal/K·mol$_{\mathbf{Mn}}$**
$\mathbf{(\Delta G^0_{298})_r}$ = $(\Delta H^0_{298})_r$ – 298*$(\Delta S^0_{298})_r$ = 8710 - 298*22.75 = **1 930 cal/mol$_{\mathbf{Mn}}$**

It is necessary to add heat to the reaction **at room temperature**, entropy increases, but **reaction is not thermodynamically probable**

$\Delta a = 2*7.17 + 6.03 – (2*6.52 + 6.60) = –9.27$ cal/K·mol$_{Mn}$
$\Delta b = [2*2.56 + 3.56 – (2*0.78 + 2.44)] \cdot 10^{-3} = 4.68 \cdot 10^{-3}$ cal/K²·mol$_{Mn}$
$\Delta c = [2*0.08 – 0.44 – (2*0.12 – 3.88)] \cdot 10^5 = 3.36 \cdot 10^5$ cal·K/mol$_{Mn}$

$$(\Delta H^0_T)_r = (\Delta H^0_{298})_r + \Delta a*(T-298) + ½\Delta b*(T^2-298^2) - \Delta c*\left(\frac{1}{T} - \frac{1}{298}\right)$$

$\mathbf{(\Delta H^0_{1000})_r} = 8710 – 9.27*702 + 2.34 \cdot 10^{-3}*(1000 \cdot 10^3 – 88.8 \cdot 10^3) – 336 \cdot 10^3* (1 \cdot 10^{-3}–3.36 \cdot 10^{-3})$
= 8710 – 6508 + 2132 + 793 = **5 127 cal/mol$_{\mathbf{Mn}}$**

$$\left(\Delta S^0_T\right)_r = \left(\Delta S^0_{298}\right)_r + \Delta a \cdot \ln\frac{T_1}{298} + \Delta b \cdot (T - 298) - \frac{1}{2}\Delta c \cdot \left(\frac{1}{T^2} - \frac{1}{298^2}\right)$$

$\mathbf{(\Delta S^0_{1000})_r}$ = 22.75 – 9.27*1.21 + 4.68·10^{-3} *702 + 1.68·10^5 *1.03·10^{-5} = 22.75 – 11.22 + 1.64 = 22.75 – 11.22 + 3.29 + 1.73 = **16.55 cal/K·mol$_{Mn}$**

$\mathbf{(\Delta G^0_{1000})_r}$ = $(\Delta H^0_{1000})_r$ – 1000*$(\Delta S^0_{1000})_r$ = 5127 – 16550 = **- 11 423 cal/mol$_{Mn}$**
Added heat is lower by 40% **at a temperature of 1000 K** then at room temperature, entropy increase is a bit lower, but the reaction **should proceed**.

To determine the minimal temperature at which $(\Delta G^0_T)_r \leq 0$ we need to know temperature dependence of rection Gibbs free energy. First approximation is linear aproximation, more exact expression is only a little bit more complicated:

$$(\Delta G^0_T)_r = -\Delta a \cdot T \cdot \ln T - ½\Delta b \cdot T^2 - ½\Delta c/T + I_H + I_G \cdot T$$

Calculation of integral constant I_H from known value of $(\Delta H^0_{298})_r$ = 8 710 cal/mol$_{Mn}$:

$$(\Delta H^0_T)_r = \Delta a * T + ½\Delta b * T^2 - \Delta c * \frac{1}{T} + I_H$$

$$8710 = -9.27*298 + 2.34 \cdot 10^{-3} * 298^2 – 3.36 \cdot 10^5/298 + I_H$$

$$I_H = 8710 + 2762 – 208 + 1128 = 12392 \text{ cal}$$

Calculation of integral constant I_G again for known $(\Delta G^0_{298})_r$ = 1 930 cal/mol$_{Mn}$:

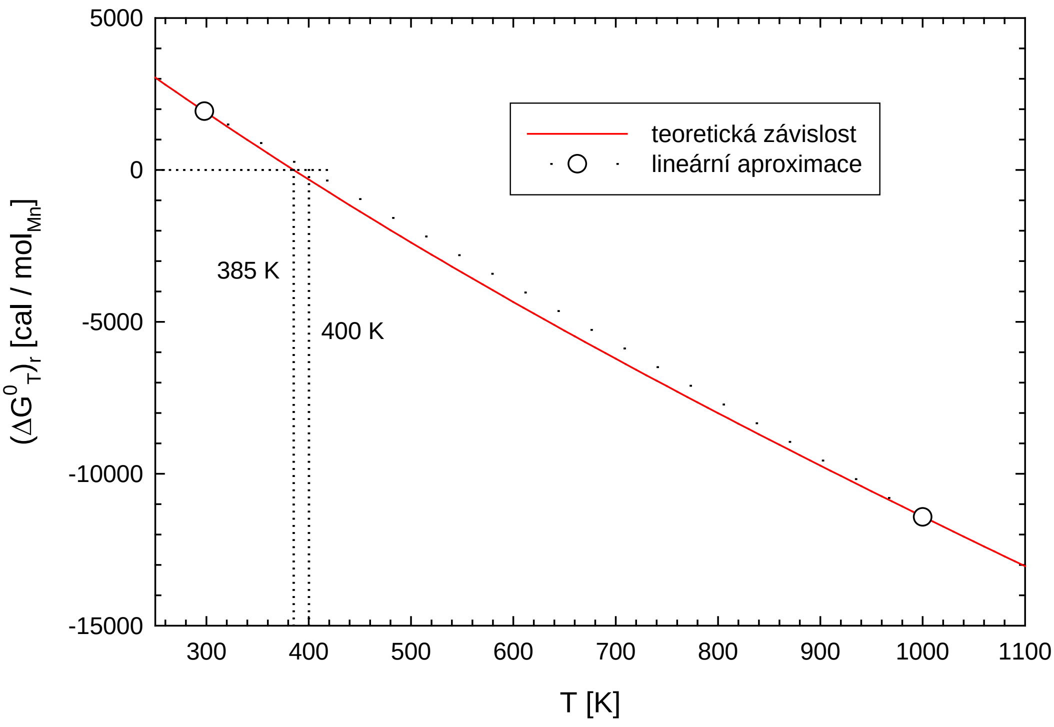
$$(\Delta G^0_T)_r = -\Delta a \cdot T \cdot \ln T - ½\Delta b \cdot T^2 - ½\Delta c/T + I_H + I_G \cdot T$$

$$1930 = +9.27*298*\ln 298 – 2.34 \cdot 10^{-3} *298^2 - 1.68 \cdot 10^5 / 298 + 12392 + I_G*298$$

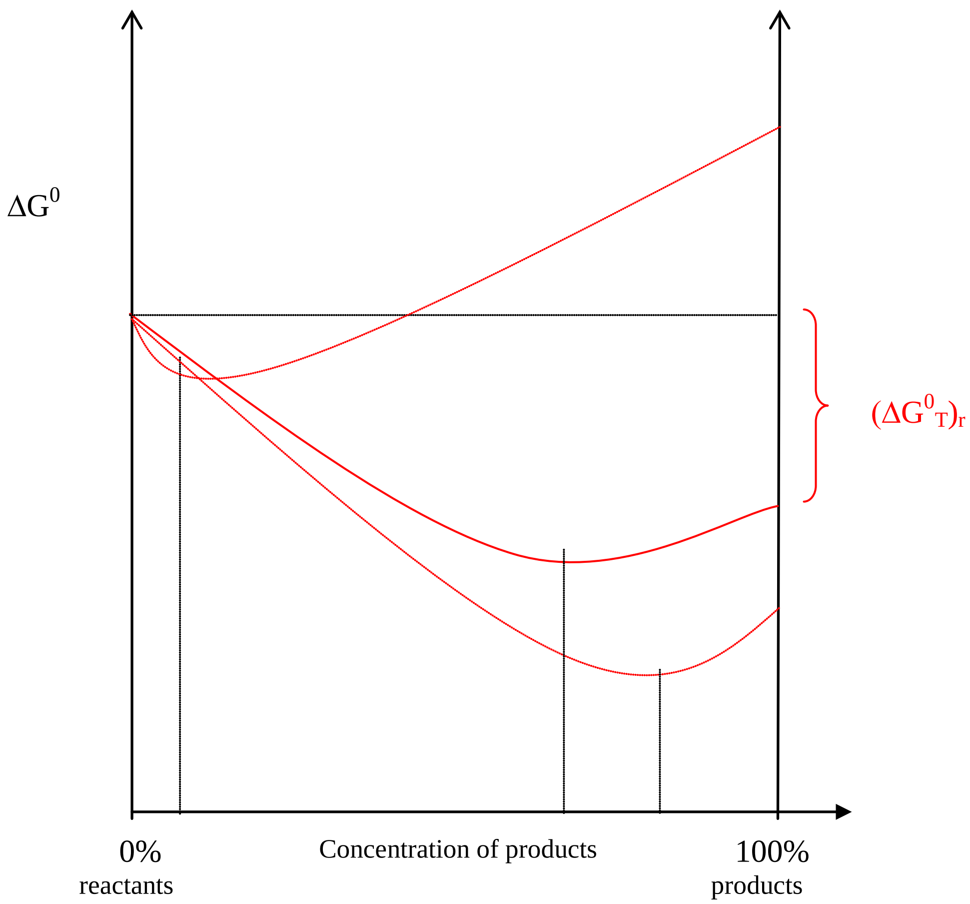
$$I_G = 1/298 * (1930 - 15738 + 208 + 564 – 12392) = -85.33 \text{ cal/K}$$

$$(\Delta G^0_T)_r = 9.27 \cdot T \cdot \ln T – 2.34 \cdot 10^{-3} \cdot T^2 – 1.68 \cdot 10^5/T + 12392 - 85.33 \cdot T$$

$\mathbf{(\Delta G^0_{1000})_r}$ = 64035 – 2340 – 168 + 12392 – 85330 = **-11 411 cal/mol$_{Mn}$**



Calculations of reaction Gibbs energies have significant practical impact. They enables estimation of conditions at which various chemical reactions are realizable.
Reaction yields are increasing with decreasing of reaction change of Gibbs free energy.



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