6.1. Introduction :

Chemical thermodynamics makes it possible to predict the evolution of the chemical reaction from the initial state (reactants) to the final state (products), whereas kinetics deals with the course of this reaction as a function of time (fast or slow). The purpose of chemical kinetics is therefore the study of velocities and mechanisms.

6.2. Definitions:

6.2.1. Initial time or zero time, t_0:

Is the start of a chemical reaction.

6.2.2. Half-reaction time, $t1_{/2}$:

Is the time it takes for half of a reaction to be complete.

6.2.3. Speed of a reaction:

*** Definition:**

The speed of a reaction is defined either in relation to the disappearance of a reactant or in relation to the appearance of a product. It is expressed in units of concentration per unit of time ($mol.\ l^{-1}.s^{-1}$); it is always positive.

-Variation of the reactant concentration is negative (the reactant disappears).

-Variation of the product concentration is positive (the product appears).

*** Determination of reaction rate:**

Either the following reaction: a A + b B $\rightarrow$ c C + d D

The v_A, v_B, v_C and v_D speeds are different because a, b, c and d can be different.

$$\mathbf{v_A = -\frac{d[A]}{dt}\ ;\ v_B = -\frac{d[B]}{dt}\ ;\ v_C = +\frac{d[C]}{dt}\ ;\ v_D = +\frac{d[D]}{dt}}$$

Either **v the reaction rate:**

$$\mathbf{v = \frac{1}{a}v_A = \frac{1}{b}v_B = \frac{1}{c}v_C = \frac{1}{d}v_D}$$

From where:

$$\mathbf{v = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}}$$

Example: $I_2 + H_2 \rightarrow 2HI$

$$\mathbf{v = -\frac{d[I_2]}{dt} = -\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[HI]}{dt}}$$

6.2.4. Speed law:

The speed of a chemical reaction is often proportional to the concentration of reactants.

$\mathbf{v_{exp} = k.\ [A]^{\alpha}.\ [B]^{\beta}}$

With:

k: being the reaction rate constant which does not depend on concentrations but varies with temperature.

α, ß: Partial orders of the reaction with respect to reactants A and B respectively.

By stating : **n = α + ß.**

n: Total or global order of the reaction.

6.3. Main factors influencing reaction rate (kinetic factors):

Kinetic factors are physical quantities that influence the speed of a reaction. These factors are: reactant concentration, reaction medium temperature and catalysts.

6.3.1. Influence of concentration (Order of a reaction):

6.3.1.1. Single-reagent system:

a. Zero order reaction (n = 0):

Consider the reaction: a. A → b. B + c. C

The kinetic equation is: $\mathbf{v} = -\frac{\mathbf{1}}{\mathbf{a}}\frac{\mathbf{d[A]}}{\mathbf{dt}} = \mathbf{k}\ [\mathbf{A}]^{\alpha}$

The rate has an order α relative to A.

$$\mathrm{v} = -\frac{1}{a}\frac{d[A]}{dt} = \mathbf{k}\ [\mathbf{A}]^{\mathbf{0}} = k \rightarrow d[A] = -\,a.k.dt \rightarrow \int_{[A]_0}^{[A]} d[A] = -a.k\int_0^t dt$$

$$[A]_t - [A]_0 = -\,a.k.t \rightarrow \mathbf{[A]_t = -\,a.k.t + [A]_0}$$

The graph$[\mathbf{A}]_{\mathbf{t}} = \mathbf{f}(\mathbf{t})$ is a straight line of slope$(-\mathbf{a.k})$ and ordinate at origin $[\mathbf{A}]_{\mathbf{0}}$ (see Figure 6.1).

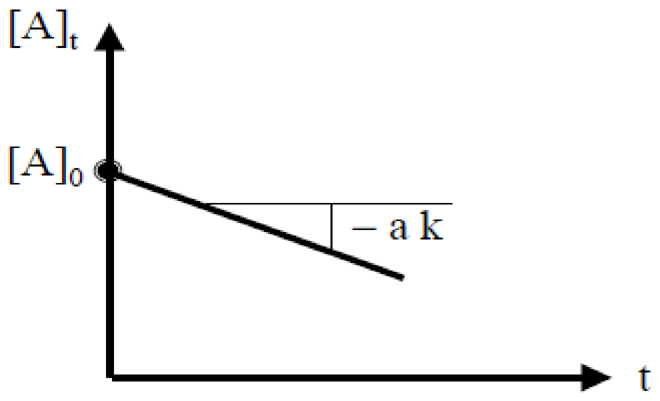


Figure 6.1. Linearized representation of [A] $_t$ as a function of time t.

*Half-reaction period or time (t1/2):

$$t = t_{1/2} \rightarrow [A] = \frac{[A]_0}{2}$$

Hence: $\frac{[A]_0}{2} = -\,a.k.t_{1/2} + [A]_0 \rightarrow a.k.t_{1/2} = \frac{[A]_0}{2}$

$$\mathbf{t_{1/2} = \frac{[A]_0}{2.a.k}}$$

*$t_{1/2}$ of a zero-order reaction depends on the initial concentration$[A]_0$.

*Unit of k is: (concentration. time^{-1}) mol. l^{-1}·s^{-1}

b. Reaction of order one (n = 1):

Consider the reaction: a. A → b. B + c. C

$$v = -\frac{1}{a}\frac{d[A]}{dt} = k\,.\,[A] \rightarrow \frac{d[A]}{[A]} = -\,a.k.dt \rightarrow \int_{[A]_0}^{[A]}\frac{d[A]}{[A]} = -\,a.k.\int_0^t dt$$

$$\left[\mathrm{Ln}\,[A]\right]_{[A]_0}^{[A]} = -\,a.k.t \rightarrow \ \mathrm{Ln}\,[A] - \mathrm{Ln}\,[A]_0 = -\,a.k.t$$

$$\mathbf{Ln\,[A] = -\,a.k.t + Ln\,[A]_0}$$

The graph $\mathbf{Ln\,[A] = f(t)}$ is a straight line of slope $(\mathbf{-a.k})$ and ordinate at origin $\mathbf{Ln\,[A]_0}$ (see Figure 6.2).

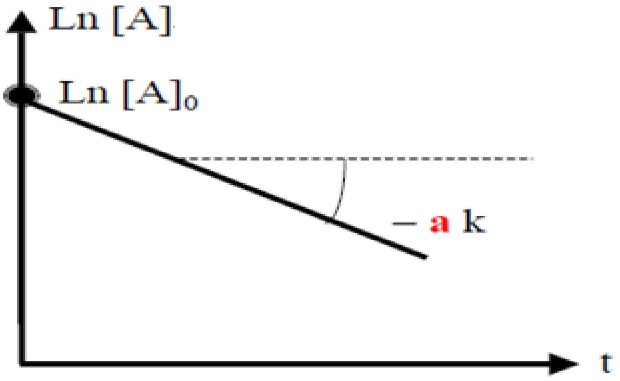


Figure 6.2. Linearised representation of Ln[A]$_t$ as a function of t.

***Half-reaction time (t1/2):**

$$t = t_{1/2} \rightarrow [A] = \frac{[A]_0}{2}$$

Hence: $\mathrm{Ln}\left(\frac{[A]_0}{2}\right) = -\,a.k.t_{\frac{1}{2}} + \mathrm{Ln}[A]_0 \rightarrow \mathrm{Ln}\left(\frac{[A]_0}{2}\right) - \mathrm{Ln}[A]_0 = -\,a.k.t_{\frac{1}{2}}$

$$\mathrm{Ln}\left(\frac{1}{2}\right) = -\,a.k.t_{\frac{1}{2}}$$

$$\mathbf{t_{1/2} = \frac{Ln\,2}{a.k}}$$

*$t_{1/2}$ of a 1st order reaction is independent of the initial concentration $[A]_0$.

*Unit of k is: (time^{-1}) s^{-1}

c. Reaction of order two (n = 2):

Consider the reaction: a. A → c. C

$$v = -\frac{1}{a}\frac{d[A]}{dt} = k\,.\,[A]^2 \rightarrow \int_{[A]_0}^{[A]}\frac{d[A]}{[A]^2} = -\,a.k.\int_0^t dt$$

$$\left[-\frac{1}{[A]}\right]_{[A]_0}^{[A]} = -\,a.k.t \rightarrow \frac{1}{[A]_0} - \frac{1}{[A]} = -\,a.k.t$$

$$\mathbf{\frac{1}{[A]_t} = a.k.t + \frac{1}{[A]_0}}$$

The graph $\frac{1}{[A]_t} = f(t)$ is a straight line of slope $(\mathbf{a.k})$ and ordinate at origin$\left(\frac{\mathbf{1}}{\mathbf{[A]_0}}\right)$ (see Figure 6.3).

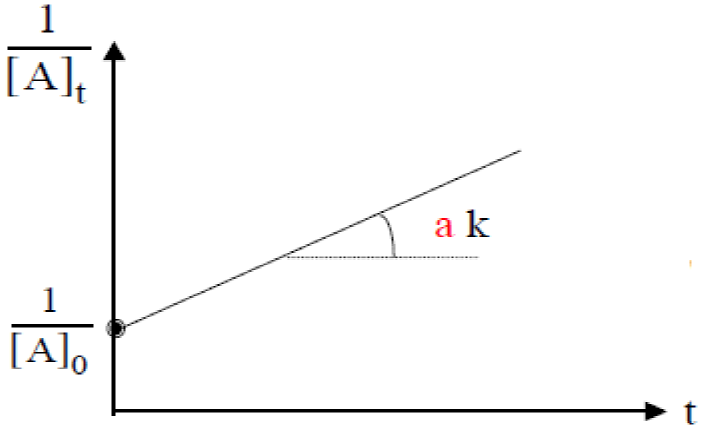


Figure 6.3. Linearized representation of 1/[A]$_t$ as a function of t.

*Half-reaction time (t1$_{/2}$):

t = $t_{1/2}$ [A] $= \frac{[A]_0}{2}$

Hence: $\frac{1}{\frac{[A]_0}{2}} = a.k.t_{\frac{1}{2}} + \frac{1}{[A]_0} \rightarrow \frac{2}{[A]_0} - \frac{1}{[A]_0} = a.k.t_{\frac{1}{2}}$

$\frac{1}{[A]_0} = a.k.t_{\frac{1}{2}}$

$\mathbf{t_{1/2} = \frac{1}{a.k.[A]_0}}$

*$t_{1/2}$ of a 2nd order reaction depends on the initial concentration$[A]_0$.

*Unit of k is: (concentration^{-1}. time^{-1}) l/mol. s

6.3.1.2. System with two reagents:

Case: $[A]_t = [B]_t$; $(\alpha = 1;\ \beta = 1)$

$A + B \rightarrow C$

t = 0 $[A]_0$ $[B]_0$ 0

t $[A]_t$ $[B]_t$ ζ $[A]_t = [A]_0 - \zeta$

Since 1 mole of A reacts with 1 mole of B; and; $[A]_0 = [B]_0 \rightarrow [A]_t = [B]_t$

$v = -\frac{1}{a}\frac{d[A]}{dt} = k\,.\,[A]_t^1.\,[B]_t^1 = k\,.\,[A]^2$

After integration: $\mathbf{\frac{1}{[A]_t} = k.t + \frac{1}{[A]_0}}$

*Partial pressure speed law:

Speed can also be expressed as a function of partial pressures

a. A $_{(gas)}$ → b. B$_{(gas)}$+ c. C$_{(gas)}$

$\mathbf{v = -\frac{1}{a}\frac{dP_A}{dt} = k\,.\,(P_A)^{\alpha}}$

***Zero-order reaction (α = 0):**

$$-\frac{1}{a}\frac{dP_A}{dt} = k\,.(P_A)^0 = k$$

$$\mathbf{(P_A)_t - (P_A)_0 = -a.k.t}$$

k in pressure. time^{-1}

***Reaction of order one (α = 1):**

$$\frac{dP_A}{P_A} = -\,a\,k\,dt$$

$$\mathbf{Ln\,(P_A)_t = -\,a.k.t + Ln\,(P_A)_0}$$

k in time^{-1}

***Second order reaction (α = 2):**

$$\mathbf{\frac{1}{(P_A)_t} = a.k.t + \frac{1}{(P_A)_0}}$$

k at pressure^{-1}. time^{-1}

6.3.2. Temperature influence:

The temperature has an influence on the speed of the reaction, this variation is given by the law of Arrhenius. The differential form of the ARRHÉNIUS equation is:

$$\mathbf{\frac{d\,LnK}{dT} = \frac{E_a}{RT^2}}$$

The integration of this equation gives the integral form of ARRHENIUS' empirical law:

$$\mathbf{K = A_0\,exp\left(\frac{-E_a}{RT}\right)}$$

With:

K: speed constant; ***it increases when temperature T rises.***

A: pre-exponential factor or frequency factor (it is independent of temperature and has the same units of k).

E_a : Activation energy(J. mol^{-1}). This is a positive quantity.

*The integration of the ARRHENIUS equation gives: $\mathbf{Ln\,k = Ln\,A_0 - \frac{E_a}{R\,T}}$

The graph $\mathbf{Ln\,k = f(\frac{1}{T})}$ is a straight line of slope $(-\,\frac{E_a}{R})$ and ordinate at origin $\mathbf{Ln\,A_0}$(see Figure 6.4).

*to T_1 :$Ln\,k_1 = Ln\,A_0 - \frac{E_a}{R\,T_1}$ ....(1)

to T_2 :$Ln\,k_2 = Ln\,A_0 - \frac{E_a}{R\,T_2}$ ....(2)

(2) – (1) → $\mathbf{Ln\left(\frac{K_2}{K_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$

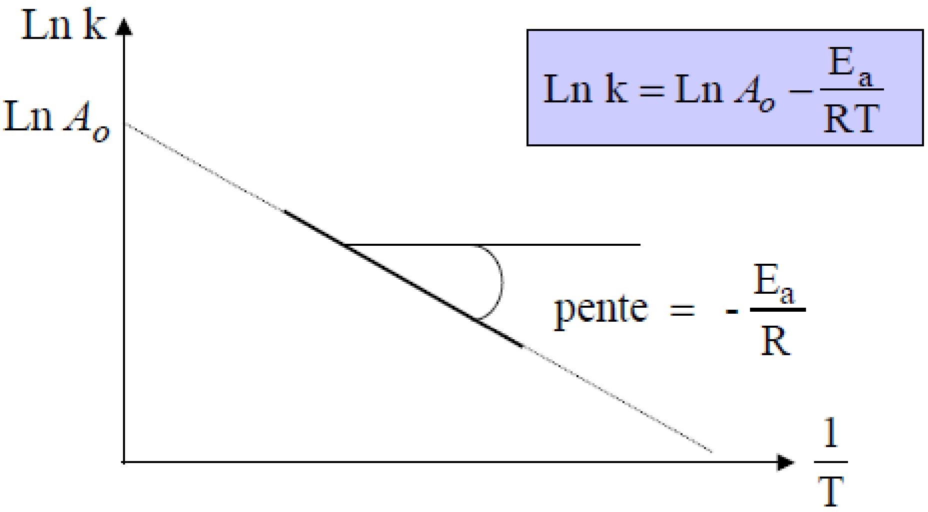


Figure 6.4. Linearized representation of LnK as a function of 1/T.

***Activation energy:**

The activation energy (Ea) is the necessary energy that the reactants must have to give the products. In other words, (Ea) is the energy barrier that reagents must cross to become products. A graphical representation of the activation energy is given in figure 6.5.

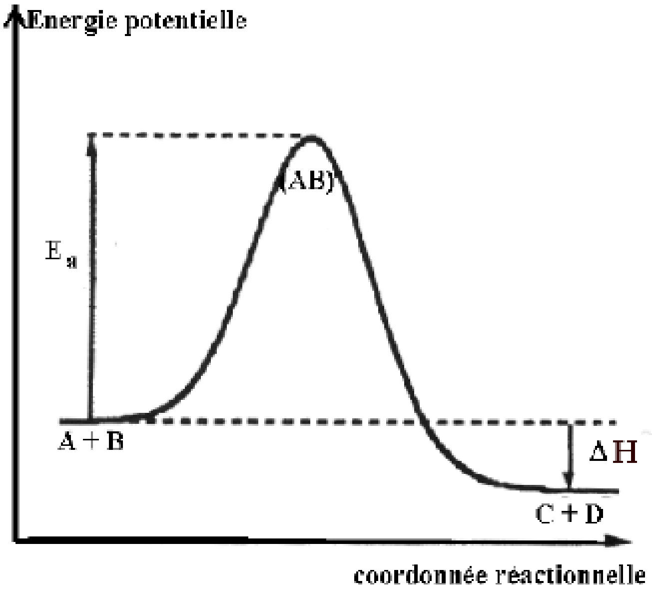


Figure 6.5. Graphic representation of the activation energy.

***Physical interpretation of the Arrhenius law:**

For bimolecular reactions, the reaction between A and B necessitates a collision between a molecule A and a molecule B. At the end of a collision, the kinetic energy of the molecules is partially transformed into the internal energy of the complex formed during the encounter. Only complexes that have stored more energy than the activation energy will **react.**

6.3.3. Influence of the catalyst:

A catalyst is a chemical that acts on the reactants of a reaction without affecting the resulting products. The role of the catalyst is to lower the activation energy and therefore increase the speed of the reaction.

A + B + catalyst → C + D + catalyst.

There are three types of catalysis:

6.3.3.1. Homogeneous catalysis:

The catalyst and reactants are therefore of the same phase. The catalyst and reactants are all gaseous or in solution (in water or other solvent).

6.3.3.2. Heterogeneous catalysis:

The reactants and catalyst are not of the same phase. The catalyst is solid and the reagents are gaseous or in aqueous solution.

6.3.3.3. Enzymatic catalysis:

Catalysis is enzymatic when the catalyst is a macromolecule of biological origin: an enzyme. They are proteins, that is to say molecules made up of a chain of several hundred amino acids.

6.4. Methods for determining the order of a reaction:

6.4.1. Integral method:

Consider the reaction: aA + bB → cC + dD

If: $[\mathrm{A}] = \mathrm{f(t)}$ or $Ln[\mathrm{A}] = \mathrm{f(t)}$ or$\frac{1}{[\mathrm{A}]} = \mathrm{f(t)}$ is a straight line, then the overall order of the reaction is 0, 1 or 2 respectively.

6.4.2. Differential method:

If the reaction admits an order: $\mathrm{v = k.[A]^{\alpha}}$

Either: $\mathbf{Lnv = Lnk + \alpha . Ln[A]}$

The curve representing$\mathbf{Lnv}$ in function of $\mathbf{Ln[A]}$ is a straight line of slope α.

6.4.3. Half-reaction time method:

Since A is the limiting reagent, the way $t_{1/2}$ depends on $[A]_0$ is characteristic of the order of the reaction in relation to A. If:

$t_{1/2}$ is proportional to [A]0	order = 0	$t_{1/2} = \frac{[A]_0}{2.a.k}$
$t_{1/2}$ is independent of the concentration	order = 1	$t_{1/2} = \frac{Ln2}{a.k}$
$t_{1/2}$ is inversely proportional to $[A]_0$	order = 2	$t_{1/2} = \frac{1}{a.k.[A]_0}$

So by studying the evolution of $t_{1/2}$ in relation to $[A]_0$ we can deduce the order of the reaction.

Example:

We are interested in the reaction: $2\ Fe^{3+} + Sn^{2+} \rightarrow 2\ Fe^{2+} + Sn^{4+}$

For a solution containing initially Fe^{3+} at 1 mol/L and Sn^{2+} à 10^{-2} mol/L, the half reaction time is 4 seconds. This time remains the same if the initial concentration of Sn^{2+} is multiplied by 2.

1. What can be concluded?

For a solution containing initially large excess Sn^{2+}, it is found that the half-reaction time doubles if we divide the initial concentration of Fe^{3+} by 2$^{.}$

2. What can be concluded?

3. Give the overall order of the reaction.

Corrected:

Velocity is expressed as: $v = k.\ [Fe^{3+}]^{\alpha}.\ [Sn^{2+}]^{\beta}$.

1. $Fe^{3+}]_0 >> [Sn^{2+}]_0$ because $[Fe^{3+}]_0 = 1$ mol/L and $[Sn^{2+}]_0 = 10^{-2}$ mol/L

Degeneration of the order in $Fe^{3+} \rightarrow v = k_{app}.\ [Sn^{2+}]^{\beta}$.

$t_{1/2}$ is independent of $[Sn^{2+}]_0 \rightarrow \boldsymbol{\beta = 1}$

2. $[Sn^{2+}]_0 >> [Fe^{3+}]_0$

Degeneration of the order in $Sn^{2+} \rightarrow v = k_{app}^{'}.\ [Fe^{3+}]^{\alpha}$.

$t_{1/2}$ is proportional to $1/\ [Fe^{3+}]_0 \rightarrow \boldsymbol{\alpha = 2}$

3. The overall order $\boldsymbol{= \alpha + \beta = 3}$.

6.4.4. Method of excess reagents (degeneration of the order):

Consider the reaction: $aA + bB \rightarrow cC + dD$

If the initial mixture contains an excess of reactant A over reactant B, then B is the limiting reactant. Therefore: $[A]$ $[A]_0$.

What's in it: $v = k.[A]^{\alpha}.[B]^{\beta} = k.[A]_0^{\alpha}.[B]^{\beta} = k_{app}.[B]^{\beta}$ with: $k.[A]_0^{\alpha} = k_{app}$

We have: $Lnv = Lnk_{app} + \beta\ Ln[B]$

The partial order β relative to B is the apparent overall order of the reaction. There is degeneration of the order in relation to the excess reactant.

By using an excess of all the reagents except one, it is thus possible to determine the partial order in relation to this only limiting reagent.

Exercise:

Consider the following reaction:

$CH_3Cl + C_2H_5ONa \longrightarrow CH_3OC_2H_5 + NaCl$

The following experimental results are obtained:

T(°C)	0	6	12	18	24	30
K (mol/l.s)	$5.6.\ 10^{-5}$	$11.8.\ 10^{-5}$	$24.5.\ 10^{-5}$	$48.8.\ 10^{-5}$	$100.\ 10^{-5}$	$208.\ 10^{-5}$

1) What is the order of reaction?

2) Does the reaction obey the law of Arrhenius?

3) Give the value of the activation energy, knowing that the constant R = 2 cal/K.mol

Correction:

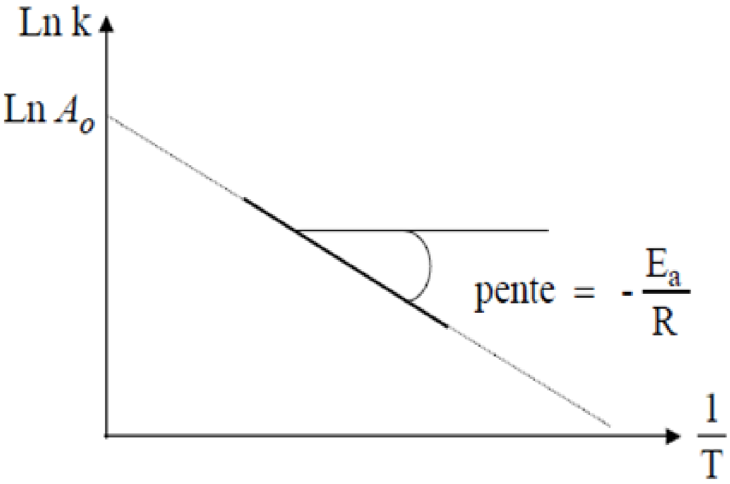
1/ The order of the reaction is zero, because the unit of **K** est **mol/L.s**

2/ Arrhenius's law:

$$K = A.\exp\left(-\frac{E_a}{RT}\right) \rightarrow \text{Ln } K = \text{Ln} A - \frac{E_a}{RT}$$

We trace: $\text{Ln } K = f(\frac{1}{T})$

$\text{Ln } K = f(\frac{1}{T})$ is a decreasing line, the reaction obeys the law of Arrhénius.



3/ Calculation of E_a:

$$\text{tg}\alpha = -\frac{E_a}{R} \rightarrow E_a = -R.\text{tg}\alpha$$

$$tg\alpha = \frac{LnK_2 - LnK_1}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{Ln\ (100.10^{-5}) - Ln\ (24{,}5\ .10^{-5})}{\frac{1}{24+273} - \frac{1}{12\ +\ 273}} = -9975{,}17$$

Therefore: E_a = -2 (- 9975.17) = 19950 cal/mol = 19.95 Kcal/mol.