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Problem solving - an interactive active method for teaching the thermokinetic concept

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Abstract: The paper describes a strategy that uses problem solving to teach the thermokinetic concept, based on student's previously established proficiency in thermochemistry and kinetics. Chemistry teachers often use this method because it ensures easy achievement of both formative and informative science skills. This teaching strategy is tailored for students that prove special intellectual resources, Olympiad participants and to those who find chemistry a potential professional route.

Keywords: problem-solving curriculum, thermodynamic and kinetic characterization of dynamic equilibrium, thermokinetic laws, linear regression.

Introduction

More and more contemporary teachers use problem-solving strategy in the currently crowed academic landscape of pre-university school, due to its proven capacity to help students reach the required formative and informative competence level.[1,2]

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In this study, an improved structure of the curricula is proposed, based on the application of notions, judgments, and reasoning from the physical chemistry area, namely from the field of thermochemistry and chemical kinetics. This method is addressed to resourceful students who demonstrate high level of intellect and strong will, also to students that prove superior academic skills, who are attracted towards chemistry, and consider it a potential professional route.

Education through problem solving is based on the situation concept: in this sense a common problem does not necessarily involve a “problem situation” because the solution is predictable.

During this process some previously learnt schemes need updating, causing contradictory, conflicting circumstances due to simultaneous perception of two realities: a cognitive one and a motivational one.[3] The student is therefore persuaded to select, hierarchize and process his previously acquired knowledge. Multiple advantages arise from this type of teaching. A few theoretical and methodological points are summarized below:

a) active and creative learning is ensured;
b) independent thinking and action taking are stimulated, together with an investigative and exploratory attitude;
c) the students are encouraged to ask questions, to update their knowledge, to formulate hypotheses and to reach conclusions;
d) the students feel the responsibility for formulating and supporting their opinions.

Problem-solving teaching begins with the joint teacher-student activity for updating previously acquired knowledge, followed by data analysis and hypothetical solution identification and formulation. Some concrete ways for bringing problem-solving into the reality of the lesson are the following: problem situation, problem questions, worksheets containing problems, movies with didactic content.[4]

The problem-solving strategy in teaching, apart from its epistemic roots, is also generated by the abundance of scientific discovery that is evident in science in general and in chemistry in particular.[5] The field of thermokinetics, as a branch of the physical chemistry, evolved as a result of Benson's research work (1976)[6] to bring together thermochemistry and chemical reaction kinetics when the equilibrium constant in known. In thermokinetics the chemical reactions for which the equilibrium constant is known are characterized from a kinetic point of view.

The technique of teaching thermokinetic concepts by using problem-solving strategy involves deducing the thermokinetics laws based on previously acquired knowledge about reversible (opposite) reactions from thermodynamic point of view.[7, 8, 9, 10] These notions connect the direct and inverse chemical reaction rate constants in opposite reactions with the equilibrium constant and also the activation energies for the direct and inverse reactions with the enthalpy of the direct reaction. The importance of thermokinetic laws application in evaluating kinetic parameters is outlined by the fact that the equilibrium constant and the enthalpy of the direct reaction are much easier to measure experimentally than the rate constants.[11]

Theoretical aspects

1. Reversible reaction

Experimentally it has been demonstrated that there are reactions that can evolve in a direct direction (forward reaction) (→), but also in a reverse direction (backward reaction) (←). This kind of reaction is a reversible reaction (reverse)[12] (Figure 1).

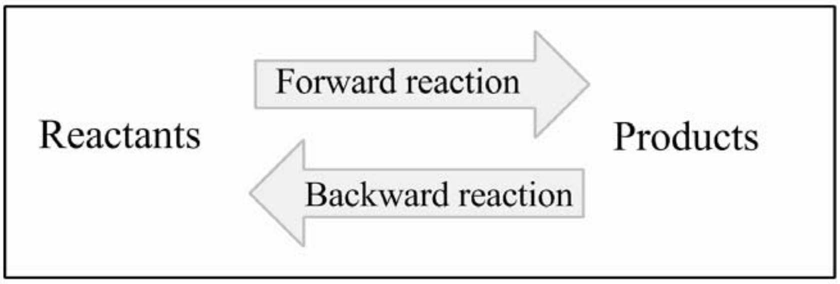

Figure 1. General scheme for reversible reaction.

Examples:

- the synthesis reaction of ammonia;

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

- the synthesis reaction of phosphorus pentachloride by the chlorination of phosphorus trichloride;

$$PCl_3\ (g) + Cl_2\ (g) \rightleftharpoons PCl_5\ (g)$$

- the synthesis reaction of hydroiodic acid;

$$I_2\ (g) + H_2\ (g) \rightleftharpoons 2\ HI\ (g)$$

- the ionization reaction of a weak acid.

$$H_2S + H_2O \rightleftharpoons HS^- + H_3O^+$$

At equilibrium all the chemicals reactants and products formed coexist (Figure 2).

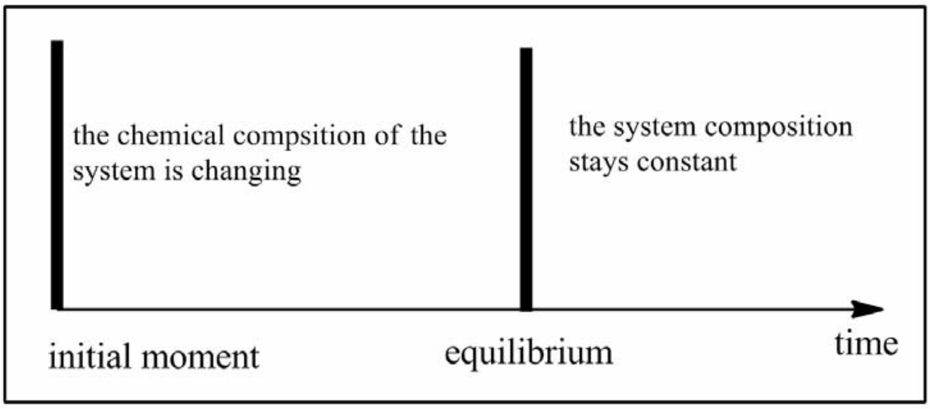

Figure 2. Time evolution of a chemical reaction.

Chemical equilibrium is established spontaneously. If the reaction conditions (concentration, temperature, pressure) remain unchanged, the system composition at equilibrium stays constant; therefore, the chemical equilibrium is stable. At equilibrium the both reactions (forward and backward) take place simultaneously with an equal rate, which confers the dynamic character of the chemical equilibrium.

2. Law of mass action of Guldberg and Waage (1864)

In 1864 two Norwegian scientists, the mathematician Cato Guldberg (1836-1902) and the chemist Peter Waage (1833- 1900), discovered the mathematical model that describes the quantitative composition of a reaction mixture at equilibrium, relation known as the law of mass action or the Guldberg-Waage's law.[13] The law is stated as following: at equilibrium, the product of molar concentration of the reaction products raised to the powers equal to their stoichiometric coefficients, divided by the product of the molar concentrations of the reactants raised to their stoichiometric coefficients, is always a constant, independently of the initial composition.

For a reaction:

$$\underbrace{r_1R_1 + r_2R_2 + r_3R_3 + \cdots\cdots + r_nR_n}_{\text{Reactants}} \rightleftharpoons \underbrace{p_1P_1 + p_2P_2 + p_3P_3 + \cdots\cdots + p_nP_n}_{\text{Products}}$$

$$K = \frac{[P_1]^{p_1} \cdot [P_2]^{p_2} \cdot [P_3]^{p_3} \cdots [P_n]^{p_n}}{[R_1]^{r_1} \cdot [R_2]^{r_2} \cdot [R_3]^{r_3} \cdots [R_n]^{r_n}} \qquad [1]$$

3. Thermokinetic laws. Benson's law

3.1. The first law of thermokinetics

For a reversible reaction:

$$A \underset{v_{-1}}{\overset{v_1}{\rightleftharpoons}} B$$

At equilibrium: $K = \frac{[B]_e}{[A]_e}$ [2]

where, v_1 represents the direct reaction rate at equilibrium and v_{-1}, the reverse reaction rate at equilibrium.

At equilibrium: $v_1 = v_{-1}$,

$$v_1 = k_1[A]_e \qquad [3]$$

$$v_{-1} = k_{-1}[B]_e \qquad [4]$$

$$k_1[A]_e = k_{-1}[B]_e \qquad [5]$$

Knowing the equilibrium constant and the rate constant of the direct reaction one may calculate the rate constant of the reverse reaction.

3.2. The second law of thermokinetics

By correlating the expression of Van't Hoff isobar of reaction with the first law of thermokinetics:

$$\left(\frac{d\ln K}{dT}\right)_p = \frac{\Delta H}{RT^2}; \qquad K = \frac{k_1}{k_{-1}} \qquad [6]$$

It results that: $\frac{d\ln k_1}{dT} - \frac{d\ln k_{-1}}{dT} = \frac{\Delta H_R^\circ}{RT^2}$ [7]

Equation [6] takes the following form by differentiating Arrhenius equation:

$$\frac{d\ln k}{dT} = \frac{Ea}{RT^2} \qquad [8]$$

$$\frac{Ea_1}{RT^2} - \frac{Ea_{-1}}{RT^2} = \frac{\Delta H_R^\circ}{RT^2} \qquad [9]$$

or: $Ea_1 - Ea_{-1} = \Delta H_R^\circ$ [10]

where, Ea_1 represents the activation energy of the direct reaction and Ea_{-1} is the activation energy of the reverse reaction.

Based on this equation, the activation energy of the reaction can be calculated from the heat of the reaction (easily determined experimentally) and the activation energy of the reaction accessible to the experimental study.

Proposed issues:

1. Verification of the first law of thermokinetics

For the reversible reaction:

$$2\ HI \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2 + I_2$$

the kinetic study of this reaction leads to the conclusion that the two opposite reactions are second order kinetic and the rate constants k_2 and k_{-2} were calculated at the temperature of 629.666 and 716 K, respectively.[14] The obtained values are presented in Table 1.

Table 1. Rate constants k_2 and k_{-2} at different temperatures.

T (K)	**Θ (°C)**	**k_2(mol^{-1}Lmin^{-1})**	**k_{-2}(mol^{-1}Lmin^{-1})**
629	356	$4.0\cdot10^{-6}$	$3.0\cdot10^{-4}$
666	393	$2.6\cdot10^{-5}$	$1.7\cdot10^{-3}$
716	443	$3.0\cdot10^{-4}$	$1.6\cdot10^{-2}$

Validate the first law of thermokinetics (equation [5]):

$$K = \frac{k_2}{k_{-2}} \qquad [11]$$

Results:

By replacing the values of the reaction rate constant from Table 1 in the first law of thermokinetics, we obtained equilibrium constant values from the kinetic data, comparable with the obtained equilibrium constant values from the experimental data. The obtained values are presented in Table 2.

Table 2. Verification of the first law of thermokinetics with the decomposition of hydroiodic acid reaction.

T (K)	ϴ (°C)	$K_{calculated}=k_2/k_{-2}$	$K_{experimental}$
629	356	$1.3\cdot10^{-2}$	$1.5\cdot10^{-2}$
666	393	$1.5\cdot10^{-2}$	$1.7\cdot10^{-2}$
716	443	$1.9\cdot10^{-2}$	$2.0\cdot10^{-2}$

Table 2 evidences a good correlation between the calculated values of the equilibrium constants using the first law of thermokinetics and those calculated from the experimental data. This relationship was verified for a large number of opposite reactions and it proved applicable, independently of the reaction kinetic order.

2. Verification of the second law of thermokinetics

For the reversible reaction:

$$2\ HI \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2 + I_2$$

Table 3 presented the necessary values for Arrhenius chart representation in order to evaluate the activation energies for the direct and the reverse reaction, based on the values from Table 1.

Table 3. The necessary values for Arrhenius chart representation.

T (K)	$1/T\cdot10^3$ (K^{-1})	k_2 ($mol^{-1}Lmin^{-1}$)	$\ln k_2$	k_{-2} ($mol^{-1}Lmin^{-1}$)	$\ln k_{-2}$
629	1.59	$4.0\cdot10^{-6}$	-12.42	$3.0\cdot10^{-4}$	-8.11
666	1.50	$2.6\cdot10^{-5}$	-10.55	$1.7\cdot10^{-3}$	-6.37
716	1.70	$3.0\cdot10^{-4}$	-8.11	$1.6\cdot10^{-2}$	-4.13

In Figure 3 and Figure 4 are presented the Arrhenius chart for the direct and the reverse reaction respectively.

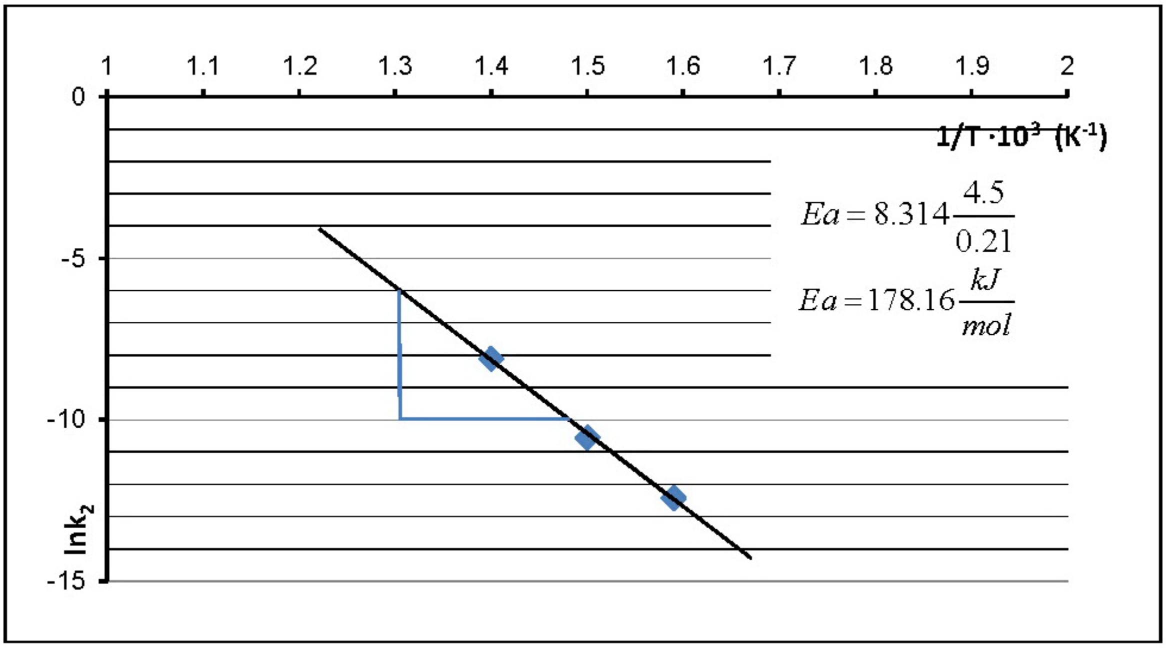

Figure 3. Arrhenius chart for the direct reaction.

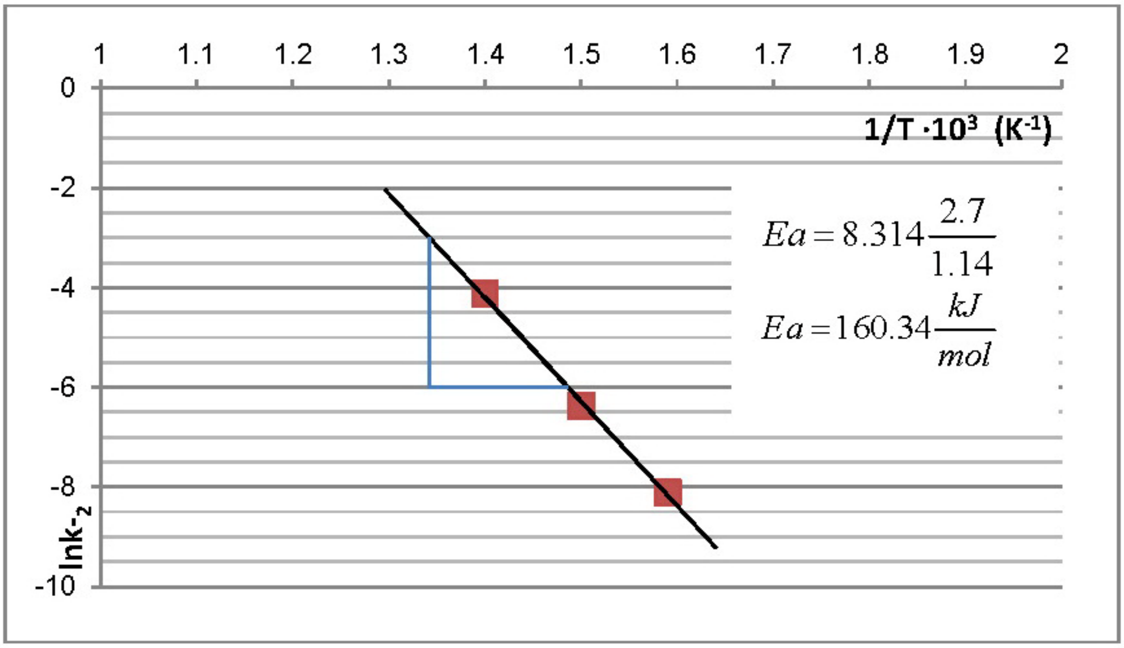

Figure 4. Arrhenius chart for the reverse reaction.

Results and Discussion

From Figure 3 and Figure 4 result that the values of the activation energies for the direct reaction and for the reverse reaction, are Ea_2 = 178.16 kJ/mol, and Ea_{-2} = 160.34 kJ/mol respectively.[14]

By replacing the values for the activation energies, Ea_2 and Ea_{-2} in the second law of thermokinetics we obtain the enthalpy of the direct reaction:

$$\Delta H_R^{\circ} = Ea_2 - Ea_{-2}; \quad \Delta H_R^{\circ} = 178.16 - 160.34; \quad \Delta H_R^{\circ} = 17.82\, {}^{kJ}\!/_{mol}$$

The calculated enthalpy value of 17.82 kJ/mol for the forward (direct) reaction is in good agreement with the obtained enthalpy value of 19 kJ/mol evaluated using thermal data from the literature[14], showing that the decomposition reaction is a weak endothermic reaction.

Conclusions

This paper completes the presented material from the thermokinetics manuals that are based on academic knowledge from thermochemistry and chemical kinetics disciplines.

The two thermokinetics laws have been presented by underlining their importance and purpose.

Two problems that verify the thermokinetics laws for a known reaction $2\ HI \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2 + I_2$ have been proposed and solved.

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