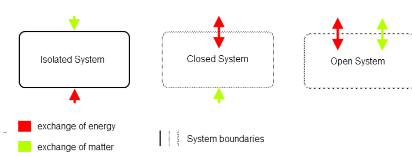
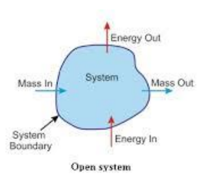
Имплементација на едноставна дидактичка секвенца за изучување на хемиската рамнотежа, без примена на ригорозни кинетички и термодинамички концепти

Љупчо Пејов, Институт за хемија

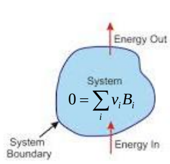
Open systems



- Two cases:

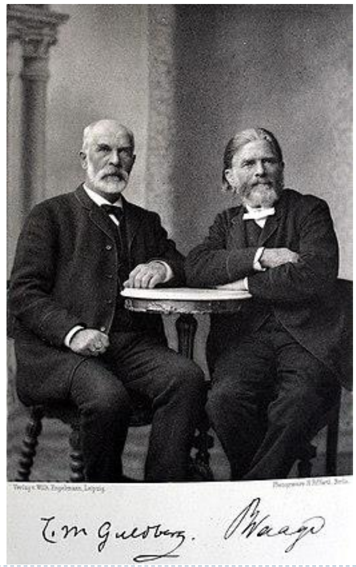


- The quantities of constituents may be changed independently (the system exchanges mass/substances with its surrounding; no chemical transformations)



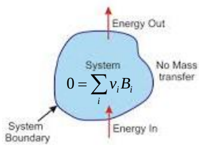
- Chemical reactions occur within the system (no exchange of mass/substances through the system's boundaries). Changes in quantities of constituents are not independent

Cato Guldberg & Peter Waage



Théophile Ernest de Donder

Single chemical reaction



$$\nu_{R_1} R_1 + \nu_{R_2} R_2 + \cdots = \nu_{P_1} P_1 + \nu_{P_2} P_2 + \cdots$$

$$\sum_i \nu_{R_i} R_i = \sum_i \nu_{P_i} P_i$$

$$0 = \sum_i \nu_{P_i} P_i - \sum_i \nu_{R_i} R_i$$

$$0 = \sum_i \nu_i B_i \qquad \begin{matrix} B_i \in \{P_i\} \Rightarrow \nu_i > 0 \\ B_i \in \{R_i\} \Rightarrow \nu_i < 0 \end{matrix}$$

$$\xi(t) = \frac{n_i(t) - n_{i,0}}{\nu_i} \qquad n_i(t) = n_{i,0} + \nu_i \xi(t)$$

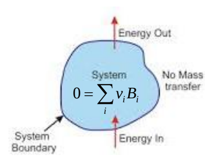
Where to start: characteristic thermodynamical functions

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_i Y_i \mathrm{d}X_i + \sum_i \mu_i \mathrm{d}n_i$$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P + \sum_i Y_i \mathrm{d}X_i + \sum_i \mu_i \mathrm{d}n_i$$

$$\mathrm{d}A = -S\mathrm{d}T - P\mathrm{d}V + \sum_i Y_i \mathrm{d}X_i + \sum_i \mu_i \mathrm{d}n_i$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \sum_i Y_i \mathrm{d}X_i + \sum_i \mu_i \mathrm{d}n_i$$



So far: analogously as in the case of an open system exchanging mass with the surroundings!!!

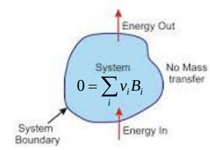
Where to start: characteristic thermodynamical functions

$$dU = TdS - PdV + \sum_i Y_i dX_i + \sum_i \mu_i dn_i$$

$$dH = TdS + VdP + \sum_i Y_i dX_i + \sum_i \mu_i dn_i$$

$$dA = -SdT - PdV + \sum_i Y_i dX_i + \sum_i \mu_i dn_i$$

$$dG = -SdT + VdP + \sum_i Y_i dX_i + \sum_i \mu_i dn_i$$



BUT!!! WHAT'S THE (BIG) DIFFERENCE???

Changes in quantities of constituents are *NOT INDEPENDENT*

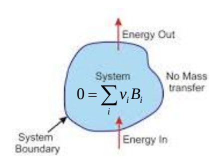
Single chemical reaction

$$dU = TdS - PdV + \sum_i Y_i dX_i + \sum_i \mu_i \nu_i d\xi$$

$$dH = TdS + VdP + \sum_i Y_i dX_i + \sum_i \mu_i \nu_i d\xi$$

$$dA = -SdT - PdV + \sum_i Y_i dX_i + \sum_i \mu_i \nu_i d\xi$$

$$dG = -SdT + VdP + \sum_i Y_i dX_i + \sum_i \mu_i \nu_i d\xi$$



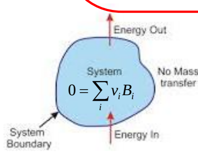
Single chemical reaction

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_i Y_i \mathrm{d}X_i + \mathrm{d}\xi \sum_i \nu_i \mu_i \qquad S, V, X = const.$$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P + \sum_i Y_i \mathrm{d}X_i + \mathrm{d}\xi \sum_i \nu_i \mu_i \qquad S, P, X = const.$$

$$\mathrm{d}A = -S\mathrm{d}T - P\mathrm{d}V + \sum_i Y_i \mathrm{d}X_i + \mathrm{d}\xi \sum_i \nu_i \mu_i \qquad T, V, X = const.$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \sum_i Y_i \mathrm{d}X_i + \mathrm{d}\xi \sum_i \nu_i \mu_i \qquad T, P, X = const.$$



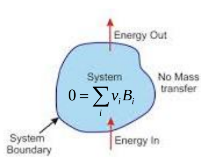
Single chemical reaction

$$\mathrm{d}U = \mathrm{d}\xi \sum_i \nu_i \mu_i \qquad S, V, X = const.$$

$$\mathrm{d}H = \mathrm{d}\xi \sum_i \nu_i \mu_i \qquad S, P, X = const.$$

$$\mathrm{d}A = \mathrm{d}\xi \sum_i \nu_i \mu_i \qquad T, V, X = const.$$

$$\mathrm{d}G = \mathrm{d}\xi \sum_i \nu_i \mu_i \qquad T, P, X = const.$$



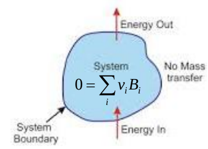
Single chemical reaction

$$\left(\frac{\partial U}{\partial \xi}\right)_{S,V,X} = \sum_i \nu_i \mu_i$$

$$\left(\frac{\partial H}{\partial \xi}\right)_{S,P,X} = \sum_i \nu_i \mu_i$$

$$\left(\frac{\partial A}{\partial \xi}\right)_{T,V,X} = \sum_i \nu_i \mu_i$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P,X} = \sum_i \nu_i \mu_i$$



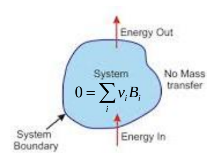
Single chemical reaction

$$-\left(\frac{\partial U}{\partial \xi}\right)_{S,V,X} = -\sum_i \nu_i \mu_i = \mathcal{A}$$

$$-\left(\frac{\partial H}{\partial \xi}\right)_{S,P,X} = -\sum_i \nu_i \mu_i = \mathcal{A}$$

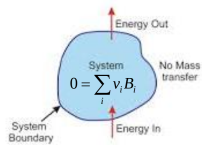
$$-\left(\frac{\partial A}{\partial \xi}\right)_{T,V,X} = -\sum_i \nu_i \mu_i = \mathcal{A}$$

$$-\left(\frac{\partial G}{\partial \xi}\right)_{T,P,X} = -\sum_i \nu_i \mu_i = \mathcal{A}$$



De Donder & van Rysselberghe

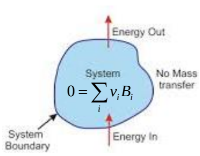
Single chemical reaction

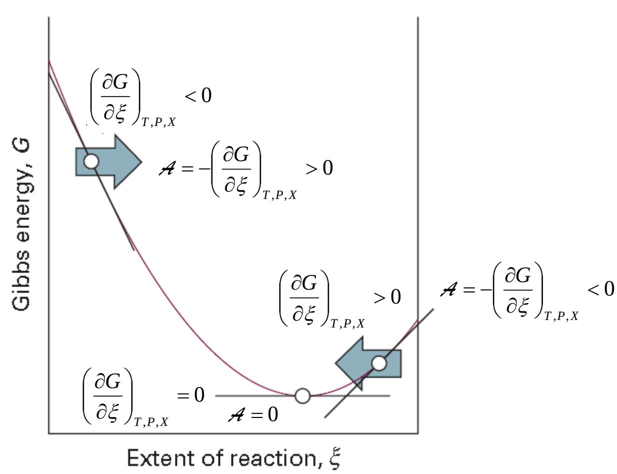


$$-\left(\frac{\partial U}{\partial \xi}\right)_{S,V,X} = -\left(\frac{\partial H}{\partial \xi}\right)_{S,P,X} = -\left(\frac{\partial A}{\partial \xi}\right)_{T,V,X} =$$

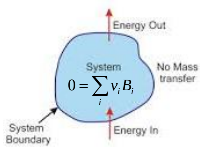
$$= -\left(\frac{\partial G}{\partial \xi}\right)_{T,P,X} = -\sum_i \nu_i \mu_i = \mathcal{A}$$

The AFFINITY

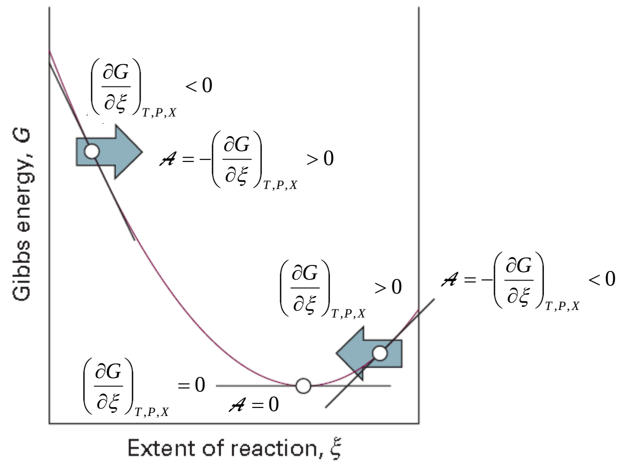




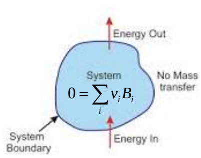
The most general thermodynamical condition for chemical equilibrium



$$\mathcal{A} = 0$$



The Reaction Gibbs energy



$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P,X} = \sum_i \nu_i \mu_i$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,X,n_{j(j\neq i)}} = \overline{G}_{\mathrm{m},i}$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P,X} = \sum_i \nu_i \mu_i = \Delta_{\mathrm{r}} G$$

A particular simple example (but yet relevant)

A ª B

$$n_{\mathrm{A}}(t) = n_{\mathrm{A},0} - \xi(t) \qquad n_{\mathrm{B}}(t) = n_{\mathrm{B},0} + \xi(t)$$

$$\mathrm{d}n_{\mathrm{A}} = -\mathrm{d}\xi \qquad \mathrm{d}n_{\mathrm{B}} = \mathrm{d}\xi$$

$$T, P, X = const.$$

$$\mathrm{d}G = \boxed{-S\mathrm{d}T + V\mathrm{d}P + \sum_i Y_i \mathrm{d}X_i} + \sum_i \mu_i \nu_i \mathrm{d}\xi$$

$$\mathrm{d}G = \mu_{\mathrm{B}}\mathrm{d}\xi - \mu_{\mathrm{A}}\mathrm{d}\xi = (\mu_{\mathrm{B}} - \mu_{\mathrm{A}})\mathrm{d}\xi$$

A particular simple example (but yet relevant)

A ª B

$$\mathrm{d}G = \mu_{\mathrm{B}}\mathrm{d}\xi - \mu_{\mathrm{A}}\mathrm{d}\xi = (\mu_{\mathrm{B}} - \mu_{\mathrm{A}})\mathrm{d}\xi$$

$$\left(\frac{\partial \mathrm{G}}{\partial \xi}\right)_{T,P,X} = \Delta_{\mathrm{r}} G = \mu_{\mathrm{B}} - \mu_{\mathrm{A}}$$

So:

- $\mu_B < \mu_A \Rightarrow \Delta_r G < 0$; A $\rightarrow$ B spontaneous
- $\mu_B > \mu_A \Rightarrow \Delta_r G > 0$; B $\rightarrow$ A spontaneous
- $\mu_B = \mu_A \Rightarrow \Delta_r G = 0$; Equilibrium

The Equilibrium Constant

$$\mathcal{A} = -\left(\frac{\partial G}{\partial \xi}\right)_{T,P,X} = -\sum_i v_i \mu_i = 0$$

$$\sum_i v_i \mu_i = 0$$

$$\mu_i = \mu_i^{\text{o}} + RT \ln a_i$$

$$\sum_i v_i \left(\mu_i^{\text{o}} + RT \ln a_i\right) = 0$$

$$\sum_i v_i \mu_i^{\text{o}} + RT \sum_i v_i \ln a_i = 0$$

The Equilibrium Constant

$$\sum_i v_i \mu_i^{\text{o}} + RT \sum_i v_i \ln a_i = 0$$

$$\sum_i v_i \mu_i^{\text{o}} + RT \sum_i \ln a_i^{v_i} = 0$$

$$\sum_i v_i \mu_i^{\text{o}} + RT \ln \prod_i \left(a_i^{v_i}\right)_{\text{e}} = 0$$

$$\ln \prod_i \left(a_i^{v_i}\right)_{\text{e}} = -\frac{\sum_i v_i \mu_i^{\text{o}}}{RT}$$

The Equilibrium Constant

$$\ln \prod_i \left(a_i^{\nu_i}\right)_{\mathrm{e}} = -\frac{\sum_i \nu_i \mu_i^{\mathrm{o}}}{RT}$$

$$\prod_i \left(a_i^{\nu_i}\right)_{\mathrm{e}} = \exp\left(-\frac{\sum_i \nu_i \mu_i^{\mathrm{o}}}{RT}\right)$$

$$K_a = \prod_i \left(a_i^{\nu_i}\right)_{\mathrm{e}} = \exp\left(-\frac{\sum_i \nu_i \mu_i^{\mathrm{o}}}{RT}\right)$$

The Equilibrium Constant

$$K_a = \prod_i \left(a_i^{\nu_i}\right)_{\mathrm{e}} = \exp\left(-\frac{\sum_i \nu_i \mu_i^{\mathrm{o}}}{RT}\right)$$

$$\sum_i \nu_i \mu_i^{\mathrm{o}} = \Delta_{\mathrm{r}} G^{\mathrm{o}}$$

$$K_a = \prod_i \left(a_i^{\nu_i}\right)_{\mathrm{e}} = \exp\left(-\frac{\Delta_{\mathrm{r}} G^{\mathrm{o}}}{RT}\right)$$

$$\Delta_{\mathrm{r}} G^{\mathrm{o}} = -RT \ln K_a$$

The Equilibrium Constant – in practice

$$K_a = \prod_i \left(a_i^{\nu_i}\right)_e$$

$$K_a = \prod_i \frac{\left(a_{P_i}^{\nu_{P_i}}\right)_e}{\left(a_{R_i}^{\nu_{R_i}}\right)_e}$$

$$K_a = \frac{a_{P_1}^{\nu_{P_1}} \cdot a_{P_2}^{\nu_{P_2}} \cdot a_{P_3}^{\nu_{P_3}} \cdots}{a_{R_1}^{\nu_{R_1}} \cdot a_{R_2}^{\nu_{R_2}} \cdot a_{R_3}^{\nu_{R_3}} \cdots}$$

The complexity of the system: included (wrapped) in the definition of the relative activity *a*.

The Reaction Quotient – out of equilibrium

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P,X} = \sum_i \nu_i \mu_i = \Delta_r G \neq 0$$

$$\mu_i = \mu_i^o + RT \ln a_i$$

$$\sum_i \nu_i \left(\mu_i^o + RT \ln a_i\right) = \Delta_r G$$

$$\sum_i \nu_i \mu_i^o + RT \sum_i \nu_i \ln a_i = \Delta_r G$$

$$\Delta_r G^o + RT \sum_i \ln a_i^{\nu_i} = \Delta_r G$$

The Reaction Quotient – out of equilibrium

$$\Delta_r G^o + RT\sum_i \ln a_i^{\nu_i} = \Delta_r G$$

$$\Delta_r G = \Delta_r G^o + RT\sum_i \ln a_i^{\nu_i}$$

$$\Delta_r G = \Delta_r G^o + RT\ln\prod_i a_i^{\nu_i}$$

$$\Delta_r G = \Delta_r G^o + RT\ln Q$$

BUT

$$\Delta_r G^o = -RT\ln K_a$$

The Reaction Quotient – out of equilibrium

$$\Delta_r G = -RT\ln K_a + RT\ln Q$$

$$\Delta_r G = RT\ln\frac{Q}{K_a}$$

So, in other words, the direction in which the reaction proceeds is determined by the ratio Q/K_a

$$\frac{Q}{K_a} < 1;\quad \Delta_r G < 0;\quad Q\uparrow;\quad \{R\}\rightarrow\{P\}$$

$$\frac{Q}{K_a} > 1;\quad \Delta_r G > 0;\quad Q\downarrow;\quad \{P\}\rightarrow\{R\}$$

Homogeneous gas-phase reaction (ideal gas mixture)

$$\mu_i = \mu_i^{o} + RT \ln \frac{P_i}{P^{o}}$$

The water-gas reaction

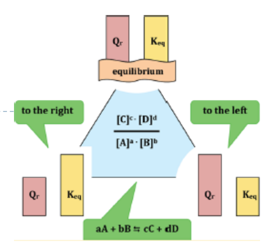
$$H_2 + CO_2 \rightleftharpoons H_2O + CO$$

$$\Delta_r G^{o} = +28.493 \text{ kJ mol}^{-1}$$

$$\mathcal{A} = -28.493 \text{ kJ mol}^{-1}$$

$$\Delta_r G = \Delta_r G^{o} + RT \ln Q \qquad Q = \frac{\dfrac{P_{CO}}{P^{o}} \dfrac{P_{H_2O}}{P^{o}}}{\dfrac{P_{H_2}}{P^{o}} \dfrac{P_{CO_2}}{P^{o}}} = \frac{P_{CO} P_{H_2O}}{P_{H_2} P_{CO_2}}$$

Активност 1



Consider the following reaction scheme:

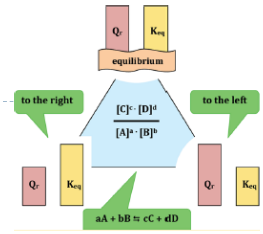
$$PhOH_{(aq)} + NH_{3(aq)} \leftrightarrows PhO^{-}_{(aq)} + NH_4^{+}{}_{(aq)}$$

and indicate if, in the two different systems described below, the molarity of each substance indicated, undergoes modifications within time.

SYSTEM 1

X	[X] (mol/dm³)	INCREASE	DECREASE	NO CHANGE	I DO NOT KNOW
$PhOH_{(aq)}$	1,50				
$NH_{3(aq)}$	1,80				
$PhO^{-}_{(aq)}$	0				
$NH_4^{+}{}_{(aq)}$	0				

Активност 1



Consider the following reaction scheme:

$$PhOH_{(aq)} + NH_{3(aq)} \rightleftharpoons PhO^-_{(aq)} + NH_4^+{}_{(aq)}$$

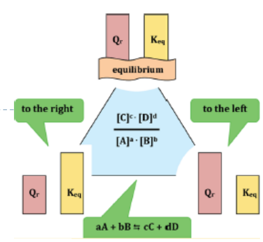
and indicate if, in the two different systems described below, the molarity of each substance indicated, undergoes modifications within time.

SYSTEM 2

X	[X] (mol/dm³)	INCREASE	DECREASE	NO CHANGE	I DO NOT KNOW
$PhOH_{(aq)}$	0				
$NH_{3(aq)}$	0				
$PhO^-_{(aq)}$	0,980				
$NH_4^+{}_{(aq)}$	3,50				

All students indicated that in system 1, the concentrations of reactants decrease, while the concentrations of products increase. Conversely, in system 2, the concentrations of reactants increase, and those of products decrease. Together with acceptable answers ("The reagents are consumed, and therefore their concentration decreases in favor of that of products"; "In the course of the reaction, the concentration of reactants decreases because products are forming, whose concentration then increases"), there are some offering

Активност 2



Consider the following reaction scheme:

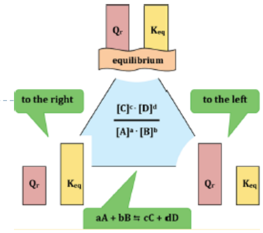
$$PhOH_{(aq)} + NH_{3(aq)} \rightleftharpoons PhO^-_{(aq)} + NH_4^+{}_{(aq)}$$

and indicate if, in the two different systems described below, the molarity of each substance indicated, undergoes modifications within time.

SYSTEM 1

X	[X] (mol/dm³)	INCREASE	DECREASE	NO CHANGE	I DO NOT KNOW
$PhOH_{(aq)}$	0,180				
$NH_{3(aq)}$	0,780				
$PhO^-_{(aq)}$	0,090				
$NH_4^+{}_{(aq)}$	0				

Активност 2



Consider the following reaction scheme:

$$PhOH_{(aq)} + NH_{3(aq)} \rightleftarrows PhO^{-}_{(aq)} + NH_4^{+}{}_{(aq)}$$

and indicate if, in the two different systems described below, the molarity of each substance indicated, undergoes modifications within time.

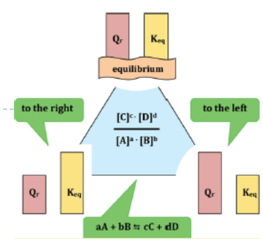
SYSTEM 2

X	[X] (mol/dm³)	INCREASE	DECREASE	NO CHANGE	I DO NOT KNOW
$PhOH_{(aq)}$	0				
$NH_{3(aq)}$	1,00				
$PhO^{-}_{(aq)}$	0,450				
$NH_4^{+}{}_{(aq)}$	5,80				

Supporting Information). For both systems, 89% of students identified the correct answer, and 11% proposed not acceptable forecasts. Examples of acceptable answers for one or the other system are "The $PhO^{-}_{(aq)}$ has no ammonium to react", "Even if one of the products is already present in a certain amount, the reaction takes place toward the right and, as soon as NH_4^+ will be produced, the reaction will also occur toward the left", "Products become reagents of opposite reaction".

For system 1, a student proposed that while reactants' concentration decreases, that of ammonium ion increases; while for phenate ion, the student did not know, trying to explain that "it depends on the yield of reaction; however, the reagents' concentration decreases because they have to form NH_4^+". As

Активност 3



Consider the following reaction scheme:

$$PhOH_{(aq)} + NH_{3(aq)} \rightleftarrows PhO^{-}_{(aq)} + NH_4^{+}{}_{(aq)}$$

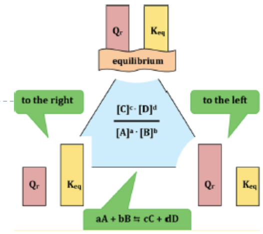
and indicate if, in the two different systems described below, the molarity of each substance indicated, undergoes modifications within time.

SYSTEM 1

X	[X] (mol/dm³)	INCREASE	DECREASE	NO CHANGE	I DO NOT KNOW
$PhOH_{(aq)}$	0,650				
$NH_{3(aq)}$	0				
$PhO^{-}_{(aq)}$	0,780				
$NH_4^{+}{}_{(aq)}$	0				

For the first system, 83% of the predictions were correct, 11% were not acceptable, and 6% did not indicate any choice.

Активност 3



Consider the following reaction scheme:

$$PhOH_{(aq)} + NH_{3(aq)} \rightleftarrows PhO^-_{(aq)} + NH_4^+{}_{(aq)}$$

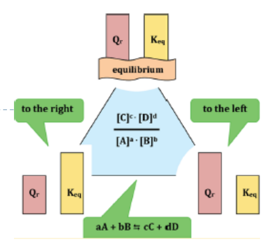
and indicate if, in the two different systems described below, the molarity of each substance indicated, undergoes modifications within time.

SYSTEM 2

X	[X] (mol/dm³)	INCREASE	DECREASE	NO CHANGE	I DO NOT KNOW
$PhOH_{(aq)}$	0				
$NH_{3(aq)}$	1,25				
$PhO^-_{(aq)}$	0				
$NH_4^+{}_{(aq)}$	2,70				

For the second system, 82% of the predictions were correct, 11% were not acceptable, and 7% did not indicate any choice. Examples of acceptable responses for one or the other system are "The chemical transformation does not happen because there are no reagents for the opposite transformations"; "we do not have a reagent, so the transformation cannot occur"; "a reaction cannot occur between two reagents if one of them is not present"". Examples of justifications for not acceptable forecasts are "State of dynamic chemical equilibrium" and "Reagents and products with lesser concentrations increase". In other cases, students did not offer any justification. In the case

Активност 4



Consider the following reaction scheme:

$$PhOH_{(aq)} + NH_{3(aq)} \rightleftarrows PhO^-_{(aq)} + NH_4^+{}_{(aq)}$$

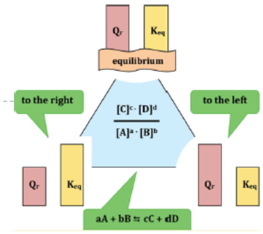
and indicate if, in the two different systems described below, the molarity of each substance indicated, undergoes modifications within time.

SYSTEM 1

X	[X] (mol/dm³)	INCREASE	DECREASE	NO CHANGE	I DO NOT KNOW
$PhOH_{(aq)}$	0,150				
$NH_{3(aq)}$	0,150				
$PhO^-_{(aq)}$	0,150				
$NH_4^+{}_{(aq)}$	0,150				

For the first system, 40% of the answers were correct. Students stated that they cannot make predictions: "It is not possible to determine anything because we do not know the yield of the reaction"; "Everything depends on the yield of the reaction, that is, the ratio between reagents and products, when the reaction is ended". This kind of assertion, discussed also with the other students, indicates that some students believe they can use the concept of yield to have an indication of the prevalence of the reactants compared to the products or vice versa. Other examples of justifications are "I do not think we have enough data" and "I do not have enough information". In this type of justification, we can see how students recognize they do not have a suitable predictive criterion. This is exactly what the worksheet aims to achieve. Forty-seven percent of the responses indicate that concentration does not change, and justifications are "The concentrations of reactants and products are equal, and therefore if the system is in equilibrium, the amount of reactants and products does not change"; "In this

Активност 4



Consider the following reaction scheme:

$$PhOH_{(aq)} + NH_{3(aq)} \rightleftarrows PhO^{-}_{(aq)} + NH_4^{+}{}_{(aq)}$$

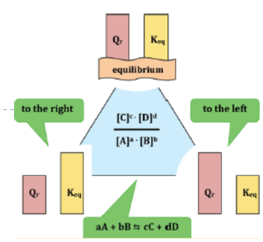
and indicate if, in the two different systems described below, the molarity of each substance indicated, undergoes modifications within time.

SYSTEM 2

X	[X] (mol/dm³)	INCREASE	DECREASE	NO CHANGE	I DO NOT KNOW
$PhOH_{(aq)}$	0,250				
$NH_{3(aq)}$	0,450				
$PhO^{-}_{(aq)}$	0,250				
$NH_4^{+}{}_{(aq)}$	0,450				

For the second system, 51% of the answers were correct and the justifications acceptable: "We do not know in which way the transformation takes place"; "We do not know whether, to get the equilibrium situation, the direct transformation or the opposite occurs". Twenty-eight percent of the answers indicate that the concentration does not change, and the justification is that the system is at the state of equilibrium. Six percent of the predictions are composite, that is, students indicate that the concentration of certain substances increases, the other decreases, and other still does not change; an example of a response is "The first two concentrations decrease because they are reagents; $PhO^{-}_{(aq)}$ increases, but I do not know if NH_4^+ increases or not because I do not know if it is at equilibrium". The second statement reveals that the student has not yet fully understood that in a state of dynamic chemical equilibrium, the opposite reactions occur in the same system; thus, the concentrations of reactants and products are interdependent.

Активност 4



Consider the following reaction scheme:

$$PhOH_{(aq)} + NH_{3(aq)} \rightleftarrows PhO^{-}_{(aq)} + NH_4^{+}{}_{(aq)}$$

and indicate if, in the two different systems described below, the molarity of each substance indicated, undergoes modifications within time.

SYSTEM 2

X	[X] (mol/dm³)	INCREASE	DECREASE	NO CHANGE	I DO NOT KNOW
$PhOH_{(aq)}$	0,250				
$NH_{3(aq)}$	0,450				
$PhO^{-}_{(aq)}$	0,250				
$NH_4^{+}{}_{(aq)}$	0,450				

After the guided discussion, the conclusion is:

to predict the evolution of a system from whatever initial state, it is necessary to have a predictive criterion.

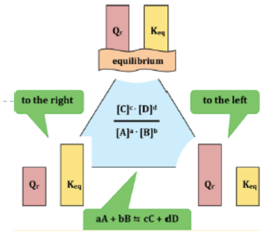
Активност 5

Consider the following reaction scheme:

$$H_{2(g)} + I_{2(g)} \rightleftarrows 2\,HI_{(g)}$$

and, based on previous considerations and on data reported in the table, propose a mathematical relationship that gives a constant value and provide an indication of what has favored the formation of the products (three attempts are possible):

	COMPOSITION OF THE SYSTEM AT THE STATE OF CHEMICAL EQUILIBRIUM (mol/dm³)			VALUES OBTAINED		
	$H_{2(g)}$	$I_{2(g)}$	$HI_{(g)}$	1° attempt	2° attempt	3° attempt
1	1,14	0,12	2,52			
2	0,92	0,20	2,96			
3	0,77	0,31	3,34			
4	0,92	0,22	3,08			
5	0,345	0,345	2,35			
6	0,86	0,86	5,86			



Twelve percent of the students were able to find the expression of equilibrium constant within the third attempt. Except in one case, which will be discussed later, the answers indicate that students do not follow a particular logic in achieving the mathematic expression. It is interesting to note that a student, who was asked to explain how they got their outcome, has derived the equilibrium constant following a reasoning similar to that of Guldberg and Waage and van't Hoff. By explaining that this reasoning is applicable only in the case of elementary reactions, this student wrote that

$$k_1 \times [H_2]^a \times [I_2]^b = k_2 \times [HI]^c$$

where $a = 1$; $b = 1$; and $c = 2$

Активност 6

Consider the following reaction scheme:

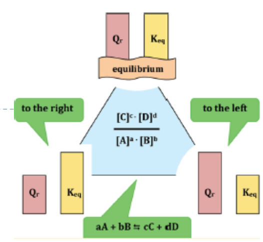
$$PhOH_{(aq)} + NH_{3(aq)} \rightleftarrows PhO^-_{(aq)} + NH_4^+{}_{(aq)}$$

and indicate if, in the two different systems described below, the molarity of each substance indicated, undergoes modifications within time.

SYSTEM 1

X	[X] (mol/dm³)	INCREASE	DECREASE	NO CHANGE	I DO NOT KNOW
$PhOH_{(aq)}$	0,150				
$NH_{3(aq)}$	0,150				
$PhO^-_{(aq)}$	0,150				
$NH_4^+{}_{(aq)}$	0,150				

Knowing that the value of the equilibrium constant of the system, at the temperature of 20°C, is equal to $K_c = 0.20$, identifie a criterion that allows you to predict the evolution of the system.



Thirty percent of students used the data of initial composition to calculate the equilibrium constant and obtained it as a numerical value. They showed that the value obtained was greater than the given value of the constant and stated: "We are not in equilibrium because the constant is 1, not 0.20. So, according to the formula, in order to have a constant equal to 0.20, the concentrations of the products must decrease"; "By calculating the constant with the data in the table, you get 1. This means that, to obtain 0.20 for the equilibrium constant, the value of the denominator must decrease, that is, the concentration of products must decrease, which also influences the denominator to increase, thus contributing to decrease the value of the constant"; "Using the formula in the initial equilibrium constant, I got $K_c = 1$. If K_c must become 0.20, then the denominator (corresponding to the reactants) must increase and the numerator (corresponding to the products) decrease; therefore, the reaction is from the right to the left". Twenty-eight percent of students failed the attempt to find a predictive criterion, and 42% did not propose any strategy.

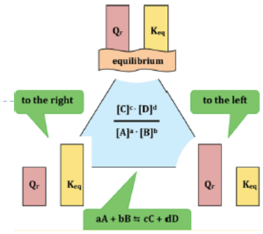
Активност 7

Consider the following two reaction schemes:

$$2NH_{3(g)} \leftrightarrows N_{2(g)} + 3H_{2(g)}$$

$$CaCO_{3(s)} \leftrightarrows CaO_{(s)} + CO_{2(g)}$$

What difference do you see between the first and the second reaction scheme?



Concerning the first question, 83% of the students reported that a difference between the first and the second reaction scheme is given by the different physical state of the substances involved. Examples of responses are: "The reactions include substances in different states"; "In the first (reaction scheme, they) are gaseous and are solid in the second one"; "In the first (reaction), there are only gaseous substances; in the second one, there are also solid substances". Three percent of students focused their attention on other differences such as different values of stoichiometric coefficients. Fourteen percent did not answer.

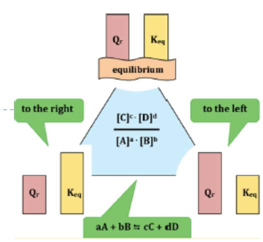
Concerning the second question, 63% correctly wrote the expression of the equilibrium constant for both the reaction schemes, while not yet neglecting, as it might be expected, the solids. Seventeen percent of students made mistakes in writing the equilibrium constants (they forgot an exponent to which elevate a concentration, used the plus sign instead of the multiplication sign, or swapped the position of concentration of the reactants with that of the products), and the remaining 20% did not write anything. The questions raised in this worksheet have a three-fold purpose: (a) to allow students to practice in writing the equilibrium constant, (b) to show that solids concentration should be omitted from the equilibrium constant, and (c) to explain that in the case of gases, the constant can be written in terms of partial pressures.

Активност 8

Consider the following reaction scheme:

$$Fe^{3+}_{(aq)} + Ag_{(s)} \leftrightarrows Ag^{+}_{(aq)} + Fe^{2+}_{(aq)}$$

The system, at the temperature of 20 °C, reaches a state of chemical equilibrium characterized by a K_c equal to 0.313. Hypothesize if, in the system described below, the molarity of the substances undergoes modifications within time.



X	[X] (mol/dm³)	INCREASE	DECREASE	NO CHANGE	I DO NOT KNOW
$Fe^{3+}_{(aq)}$	$7{,}32 \cdot 10^{-2}$				
$Ag_{(s)}$	0				
$Ag^{+}_{(aq)}$	$1{,}00 \cdot 10^{-1}$				
$Fe^{2+}_{(aq)}$	$1{,}50 \cdot 10^{-1}$				

Forty-six percent of students thought that it must be a chemical change. Examples of students' answers are: "a reaction can only take place from the right to the left, as there is no solid silver"; "The reaction takes place to the left"; "$Q_r < K_c$; therefore, the transformation takes place toward the right". Ten percent of students correctly pointed out that, even if the comparison between Q_r and K_c let them suppose that the direct transformation should occur, in reality, by missing one of the two reactants, the forecast is meaningless. Forty-four percent of students did not answer. Most of the students' answers, combined with the high percentage of students who did not answer, show that they have many difficulties in correctly predicting the evolution of the systems. Therefore, activities of this kind are essential to help them to face difficulties and to develop a critical thinking. The conclusion proposed by the teacher was: "the criterion of comparison between K_c/Q_r has limits. Therefore, before accepting, forecasts must be evaluated in light of the actual state of the system".

THANK YOU FOR YOUR TIME AND ATTENTION

QUESTIONS AND COMMENTS ARE WELCOME!