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Arrheniusan activation energy of separation for different parameters regulating the process

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Abstract: The Arrhenius model, that relates the activation energy with the kinetic constant and process temperature, was applied for flotation as a separation process, and next was extended to other incentive parameters such as the frother concentration, NaCl content and hydrophobicity. It was shown that determination of the activation energy caused by other incentive parameters (i.e. particle size, surface potential) was also possible. The units of the activation energy depend on the type of the separation process and incentive parameter. For contact angle regulating flotation the activation energy unit is mJ/m^2 , while for the frother concentration is J. It is known that instead in joules, the activation energy can also be expressed in J/mol and in kT or RT units, where k is the Boltzmann constant, R gas constant and T is absolute temperature in kelvins. Even though different formulas of the specific Gibbs potential were used for calculation of activation energy caused by various incentive parameters, there was generally a good agreement between the extend of changes of the first order kinetic constants of the process and activation energy value. It was found that for flotation of copper-bearing carbonaceous shale the activation energy was equal to 1.1 kT for NaCl as the incentive parameter, 3.0 kT for temperature and 32.7 kT for butyl diethylglycol ether used as a flotation frother. For methylated quartz the hydrophobicity-induced activation energy was 42 mJ/m^2 for contact angle as the incentive parameter.

Keywords: separation, activation energy, flotation, Gibbs potential, Arrhenius plot, incentive parameters

1. Introduction

A separation process is a thermodynamic and kinetic phenomenon. Many features of separation are similar to chemical reactions, therefore the same approaches for delineation and characterization of separation can be used. Fig. 1 shows flotation, one of many processes, in which a particle interacts with a bubble forming a product, that is bubble-particle aggregate, which due to interplay of different forces floats, leading to its separation from the process medium.

Separation proceeds with a certain rate v_1

$$v_1 = h_1 \cdot c_p \cdot c_b \quad (1)$$

and partially into the reverse direction with the rate v_2

$$v_2 = h_2 \cdot c_{p-b} \quad (2)$$

where h_1 and h_2 are proportionality constants, while symbols c_p , c_b and c_{p-b} stand for concentration of particles, bubbles, and particle-bubble aggregates, respectively.

Initially, until equilibrium is reached, $v_1 > v_2$. At the equilibrium, both rates are identical ($v_1 = v_2$), and then

$$K_v = h_2/h_1 = c_{p-b}/(c_p \cdot c_b) \quad (3)$$

where K_v is the equilibrium constant. When bubbles concentration c_b is constant, then $K_v \cdot c_b = K$. The concentration of bubble-particle aggregates and non-floating particles can be recalculated into recovery R . Then, the equilibrium constant is

$$K = R_{max} / (1 - R_{max}) \tag{4}$$

where R_{max} is the maximum (ultimate) recovery of the separation process expressed in the 0-1 scale.

The equilibrium constant K and R_{max} are equivalent thermodynamic measures of separation. However, when the process is regulated with one of different incentive parameters such as temperature, particle size, frother concentration etc., and also when the process is not at equilibrium but is stationary (continuous, steady state), an additional parameter characterizing the incentive parameter has to be taken into account. This can be done by using the Gibbs potential of a species i taking part in the process, that is μ_i , defined as (Drzymala et al., 1979)

$$\mu_i = \mu_i^0 + \sum \mu_k = \mu_i^0 + kT \ln c_i + kT \ln(c/c_0) - F\psi_0 \dots \tag{5}$$

where k is the Boltzmann constant, T absolute temperature in kelvins (K), μ^0 Gibbs standard potential of a species taking part in the process (in our case bubble, particle or particle-bubble aggregate), while the additional terms, which can be called the specific Gibbs potentials or μ_k , reflect the influence of different incentive parameters on the whole Gibbs potential μ_i . In Eq. 5 ψ_0 stands for the surface electrical potential in volts, while c is, for instance, frother concentration as the incentive parameter and c_0 is then a reference concentration of the frother. Specific formulas for the selected specific Gibbs potentials influencing separation processes are given in Table 1.

It is well known that the standard Gibbs free energy change ΔG^0 (in J) of a process depends on the standard Gibbs potentials

$$\Delta G^0 = \mu_{p-b}^0 - \mu_p^0 - \mu_b^0 = -kT \ln K. \tag{6}$$

and relates ΔG^0 with K , because at equilibrium

$$\sum v_i \mu_i = 0 \tag{7}$$

where v_i is the stoichiometry index (- for substrates).

The relation between changing K with the incentive parameter change, in principle, can be derived basing on Eqs 5-7. However, it has not been done so far enough deeply theoretically and it also requires verification with experiment data. Therefore this issue will be addressed in the future.

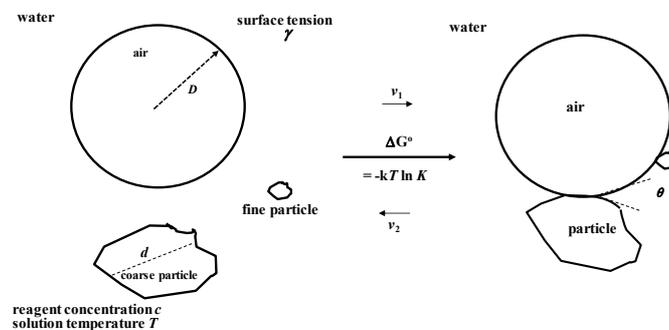


Fig. 1. Flotation as a separation process. In the figure, k denotes the Boltzmann constant and K is the process equilibrium constant for “reaction” particle+bubble=particle-bubble aggregate or shortly $p+b=p-b$.

Table 1. Selected specific Gibbs potential of incentive parameters influencing separation process

Specific Gibbs potential, μ_k	Parameter	Formula
Chemical, μ_c	reagent concentration c	$kT \ln (c/c_0)$
Physical, μ_p	particle size d	$kT \ln (d/d_0)?$
Thermal, μ_T	system temperature T	kT
Capillary, μ_t	contact angle θ	$\gamma(1-\cos\theta)$
Electrical surface potential, μ_ψ	electrical surface potential ψ_0	$kT \ln (c \cdot \exp(F\psi_0/RT)/c_0)$

The thermodynamics and kinetics of separations are interconnected. This is well visible when the separation process is characterized by a kinetic curve in the form of recovery versus time, up to the

region when the ultimate recovery R_{\max} is obtained (Fig. 2). Then, mathematical equations are used to relate R , R_{\max} and time t via the so-called rate constants. Many separations follow the first order kinetics:

$$R = R_{\max}(1 - e^{-k_1 t}) \quad (8)$$

where k_1 is the first order kinetic constant. Fig. 2 indicates not only R and R_{\max} but also physical meanings of other kinetic parameters of the first order processes including separation half-time $t_{1/2}$, initial slope $R_{\max} \cdot k_1$ and process local kinetic rate dR/dt .

Various parameters, through their specific Gibbs potential μ_x , differently change the outcomes of the separation process. The impact of temperature T as the regulating parameter on the separation process can be characterized by the so-called activation energy E_a as proposed by Arrhenius (1889):

$$k_n = A_n \cdot e^{-E_a/kT} \quad (9)$$

where k_n is the rate constant of a given order and A_n pre-exponential factor. The activation energy (E_a) can be expressed in joules (J) or kT units and k is the Boltzmann constant. For chemical reactions the Boltzmann constant is replaced with the universal gas constant R and then E_a is given in either RT or energy-per-mol units. The activation energy is determined by measuring changes in the kinetic constant, which must well approximate the separation process with time and temperature T . Symbol T stands for absolute temperature and is expressed in kelvins (K).

As can be seen in Eq. 9, the unit of the pre-exponential factor A is identical as the unit of the rate constant. When the reaction follows the first order, the unit of both k and A is 1/time. It is accepted that the kinetic constant (k) indicates the number of collisions that result in a reaction per unit time, A is the number of collisions per unit time occurring with the proper orientation to react, while $\exp(-E_a/kT)$ is the probability that any given collision will result in the reaction.

A similar approach for evaluation of the barrier energy was proposed by Evans and Polanyi in 1935 (Polanyi, 1987; Chapman and Cowling, 1991) in which A_n was differently defined and also depended on temperature, while E_a was named the Gibbs energy of activation (ΔG^\ddagger).

In the opinion of this author the Arrhenius approach can be extended to other-than-temperature incentive parameters. It is proposed that the general arrheniusan equation is then

$$k_n = A_n \cdot e^{-E_a/\mu_x} \quad (10)$$

where μ_x is a specific Gibbs potential for a given incentive parameter. The formulas for selected μ_x 's were given in Table 1. To determine E_a of a separation process for a selected incentive parameter, Eq. 10 and experimental kinetic data are needed. This will be considered in the next sections of this paper.

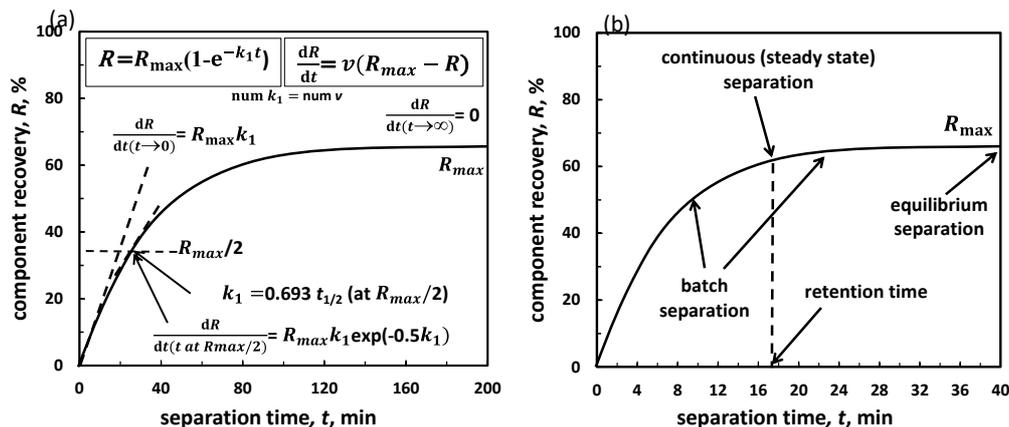


Fig. 2. Separation which follows the first order kinetics reaching equilibrium (ultimate) recovery at R_{\max} : (a) mathematical relations between parameters (Drzymala and Kowalczuk, 2018), (b) comparison of batch, steady state and equilibrium separations. Meanings of most parameters are given in the text. v is the first order specific rate, while notation $\text{num } k_1 = \text{num } v$ means that k_1 and v are numerically equal

2. Applications of the Arrhenius equation for temperature as separation incentive parameter

The arrheniusan procedure of determination of the activation energy (E_a) with temperature as the incentive parameter was used in numerous papers involving chemical reactions (Craig and Chase,

2012), hydrometallurgical processes (Feng et al., 2015; Yu et al., 2018.), pyrolysis of cellulose (Patnaik and Goldfarb, 2016) and food deterioration (Petrouet et al., 2002). In this work, to determine the temperature induced activation energy (E_a) for flotation of copper-bearing shale with a frother, the following Arrhenius equation

$$k_1 = A \cdot e^{-E_a/kT} \tag{11}$$

was used, because the process followed the first order kinetics (Fig. 3). The calculated temperature-induced activation energy was ~ 3 kT. Small changes of k_1 from about 0.1 to 0.2 (min^{-1}) indicate that temperature insignificantly improves flotation of the investigated shale. As a result E_a , a measure of the experimental line slope, expressed in kT units, is also small (~ 3 kT).

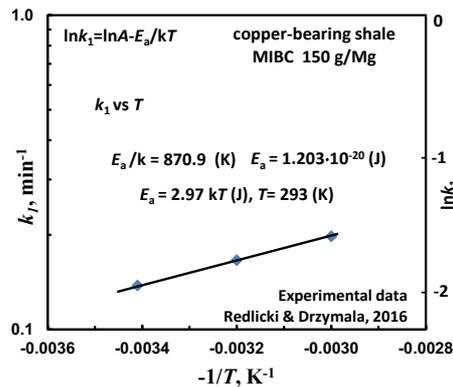


Fig. 3. Arrheniusan plot for influence of temperature on shale flotation rate in the form of 1st order rate constant (k_1). Temperature-induced activation energy was 2.97 kT. Experimental data adopted from Redlicki and Drzymala (2017). Scale on the left hand side is logarithmic while the scale on the right hand side is $\ln k_1$, that is useful for E_a (line slope) calculations

3. Applications of the Arrhenius-type equation for frother concentration as the incentive parameter

Since the specific Gibbs potential for reagents concentration is $\mu_x = kT \ln (c/c_0)$, where c is the concentration of frother and c_0 is the frother reference concentration, the Arrhenius equation in this case is

$$k_n = A_n \cdot e^{-E_a/kT \ln(c/c_0)} \tag{12}$$

Both frother concentration c and frother reference concentration c_0 must be expressed in the same unit, for instance mole/ dm^3 , g/ dm^3 , g/Mg, mole fraction etc.

The arrheniusan plot for determination of the activation energy, when flotation of shale is regulated with the frother concentration and when the rate of the process follows the 1st order kinetics ($k_n = k_1$), is given in Fig. 4. The frother concentration induced activation energy (E_a) of the considered process is 32.7 kT.

A relatively high value of E_a equal to 32.7 kT indicates that the considered frother, applied as an incentive flotation parameter, significantly improves flotation of investigated shale. This statement is supported by observation that k_1 changes 10-fold (Fig. 4) in the case of using frother concentration in comparison to 2-fold k_1 increase due to temperature change (Fig. 3). It should be noticed however, that the temperature-induced activation energy cannot be directly compared with frother concentration-induced activation energy because different formulas were used for the calculations.

The E_a of other frothers can be evaluated in the same manner.

4. Applications of the Arrhenius-type equation for salt concentration as incentive parameter

Many salts increase particles recovery in flotation (Paulson and Pugh, 1996; Pugh, et al., 1997; Laskowski et al., 1991; Ozdemir, 2013; Zhang, 2015). Copper-bearing carbonaceous shale flotation is improved with increasing concentration of sodium chloride, even though no organic frother and no collector is used (Ratajczak, 2017). The arrheniusan plot for such flotation is shown in Fig. 5. The reference NaCl

concentration c_0 was chosen as 5 M, instead of typical 1 M, due to difficulties in logarithmic calculations when the c/c_0 value is close to 1.

The activation energy for the considered flotation, calculated using Eq. 12, is small and equal to 1.1 kT, regardless of the Cu and C_{org} content in the used shale samples (Fig. 5). It means that the applied NaCl insignificantly improves the flotation of the investigated shale. Small E_a values of the salt-induced activation energy result from only 2-fold change of the rate constant k_1 (Fig. 5).

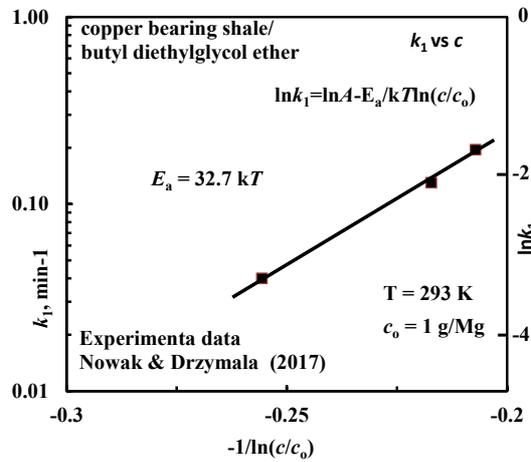


Fig. 4. Arrheniusan plot for influence of frother concentration on shale flotation rate in the form of 1st order rate constant (k_1). Frother concentration induced activation energy of the considered process is 32.7 kT. Experimental data adopted from Nowak and Drzymala (2017)

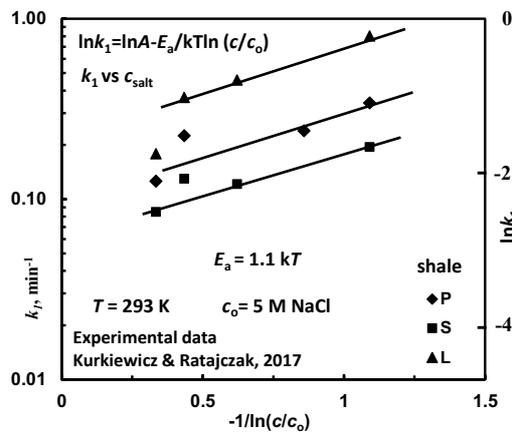


Fig. 5. Arrheniusan plot showing influence of NaCl on the flotation rate (in the form of 1st order rate constant k_1) of different copper-bearing shales samples. The salt-induced activation energy of considered process is 1.1 kT. Experimental data adopted from Kurkiewicz and Ratajczak (2017). Cu and C_{org} content in the shale samples (P: 0.83% Cu, 5.34% C_{org} ; S: 0.58% Cu, 0.55% C_{org} ; L: 1.13% Cu, 7.45% C_{org})

5. Applications of the Arrhenius-type equation for contact angle as incentive parameter

For calculation of the activation energy for flotation induced by increasing hydrophobicity, measured by the contact angle, the following equation was used:

$$k_n = A_n \cdot e^{-\frac{E_a}{\gamma(1-\cos\theta)}} \quad (13)$$

Eq. 13 is a modification of Eq. 10, in which is replaced with (Laskowski, 1986, 1989):

$$\mu_x = \mu_f = \Delta G_{\text{flotation}} = \gamma(1-\cos\theta) \quad (14)$$

that is with the Gibbs potential of flotation, that depends on the contact angle (θ) (Fuerstenau and Raghavan, 2007).

The calculated, by means of Eq. 13, hydrophobicity-induced activation energy E_a for quartz flotation is 42 mJ/m² (Fig. 6). It seems to be quite a high number and it results from about 15-fold increase of the first order kinetic constant of quartz flotation. It means that the increasing contact angle of quartz, regulated by SiO₂ surface methylation, significantly improves flotation.

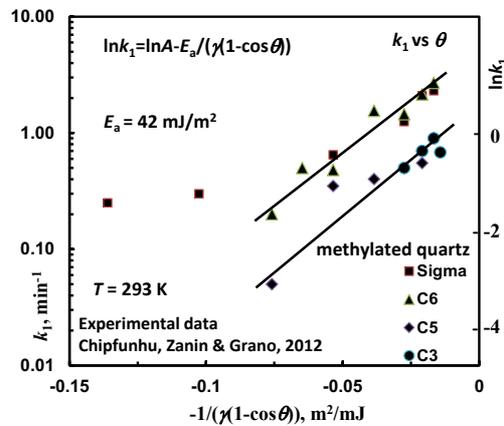


Fig. 6. Arrheniusan plot showing the influence of contact angle on flotation rate in the form of 1st order rate constant (k_1) of methylated quartz. The hydrophobicity-induced activation energy of the considered process is 42 mJ/m². Experimental data adopted from Chipfunhu et al. (2012)

6. Conclusions

The Arrhenius model of activation energy determination, which is based on relating the kinetic constant with temperature, can be also used for separation processes as well as extended for other incentive parameters such as the reagent concentration, hydrophobicity, surface charge. The linearity of the arrheniusan plot for different incentive parameters, presented in this paper as examples, seems to be reasonable. More separation cases should be considered in the future to confirm further the applicability of the Arrhenius model and proposed equations of the specific Gibbs potentials for determinations of the incentive parameter-induced activation energy.

Even though different formulas were used for calculation of activation energy, there was a good agreement between k_1 changes and E_a values, that is the numerical value of the incentive parameter-induced activation energy (E_a) was generally proportional to the extent of change of the first order kinetic constant (k_1).

7. Meaning of the most important symbols of parameters, constants and SI units used in the paper

E_a – activation energy

K – kelvin (SI unit)

K – equilibrium constant (parameter)

k – the Boltzmann constant (universal constant)

k – rate constant (parameter)

T – absolute temperature (parameter)

ΔG° – standard Gibbs free energy change ($\Delta G^\circ = \mu_{p-b}^\circ - \mu_p^\circ - \mu_b^\circ = -kT \ln K$)

μ_i – Gibbs potential of a species taking part in the process treated as a chemical reaction

μ_i° – standard Gibbs potential

μ_x – specific Gibbs potential resulting from application of an incentive parameter

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