

RATE OF COMPONENTS EVAPORATION FROM SULFURIC ACID  
SOLUTION DURING ITS CONCENTRATING IN AIR FLOW*Vladimir Lukashov<sup>1</sup>\*, Sergey Romanko<sup>1</sup>, Sergey Timofeev<sup>1</sup>, Alexander Protsenko<sup>1</sup>*

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**Abstract.** A method of experimental determination of components evaporation rate from a sulfuric acid solution during its concentrating in the flow of neutral gas is proposed. Using this methodology, the dependence of the evaporation rate on the composition of the acid solution is set. The critical value of the weight fraction of water in the solution was found at which the character of this dependence changed. An empirical equation for the approximate calculation of the evaporation rate of components from solution in the air flow was obtained.

**Keywords:** sulfuric acid, concentration, evaporation rate, neutral gas, monohydrate.

## 1. Introduction

Sulfuric acid is widely used in various industries. Consequently, a large amount of used sulfuric acid, usually diluted, is formed. For example, in the production of cellulose nitrate over 20 tons of dilute sulfuric acid per ton of cellulose nitrate is formed, which from an economic and ecological standpoint requires concentrating [1].

The process of sulfuric acid concentrating involves the removal of water by heating through the wall of the device or by the direct contact of the gas heat medium with the acid [2]. The most widely used is the second method, wherein the acid is heated by bubbling through it of a high-temperature (1073–1173 K) mixture of air and flue gases produced by burning of heavy fuel oil or natural gas. A more promising method for small-scale production in terms of energy consumption and the consumption of scarce fuels is a concentration method wherein the acid is heated through the wall of the device and through the layer of acid a gas neutral to its components, for example air, is bubbled [3]. This method enables to concentrate at a temperature below the acid boiling point and, consequently, use the low-temperature heat medium. In all

these cases, for the calculation and modeling of the process of concentrating, it is necessary to know the evaporation rate of components from solution of sulfuric acid as the total specific vapor flow of monohydrate  $\text{H}_2\text{SO}_4$  and water ( $\text{kg}/\text{m}^2\cdot\text{s}$ ).

It is known that the evaporation rate of any component of solution depends on the content of this component in the liquid phase [4]. But such theoretically obtained relations are applicable only to evaporation in a vacuum [5]. Upon evaporation into gas phase, interphase mass transfer, and especially evaporation into a neutral (inert) gas should be taken into account [6, 7]. The difficulty of this process does not allow to describe it without using experimental data.

The task of this paper is to establish based on experimental studies empirical dependence of evaporation rate of components from sulfuric acid solution on its composition by concentrating in a flow of neutral gas (air).

## 2. Experimental

### 2.1. Research Method

Investigations were carried out under laboratory conditions on an installation different from conventional simple distillation installation by applying a multi-neck glass flask in one neck of which a tube was placed. By this tube air was blown into the flask from micro-compressor through the air preheater and the rheometer. The installation was equipped with thermometers to measure the temperature of acid in the flask and the temperature of air supplied into the flask.

During the experiments the flask was filled with  $300\text{ cm}^3$  of sulfuric acid with defined concentration, which was heated using a heating mantle to a certain temperature, which was then kept constant. At this initial volume of acid a change in its level occurred within middle portion of the flask, which allowed us to consider the evaporation surface as constant (difference between the mean value surface area and its value for the upper and lower levels did not exceed 2 %). The heating rate of

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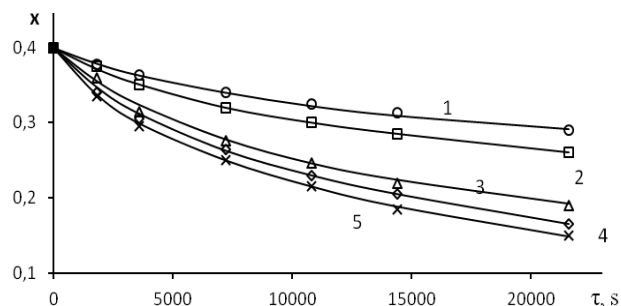
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acid to a constant temperature in all cases was approximately the same. To determine the evaporation surface, experiments were carried out without air bubbling through the acid and in the conditions when it was passed over the free surface of the acid and leaving the flask through the cooler. The values of the process parameters in the experiments varied in the range: temperature of the acid,  $t_a$ , from 373 to 473 K; air flow rate,  $V$ , from 0.5 to 5.0 dm<sup>3</sup>/s, which corresponds to its conditional rate,  $v$  (flow rate at the evaporation surface area) from 0.00106 to 0.0106 m/s; air temperature,  $t_g$ , from 293 to 473 K; an initial acid concentration,  $C_0$ , from 60 to 80 %, corresponding to an initial weight fraction of water in the acid,  $x_0$ , from 0.4 to 0.2 (weight fraction of water in the acid used for the convenience of subsequent calculations). The concentrating of the acid was carried out for time periods ranging from 1800 s (0.5 h) to 21600 s (6 h). At the end of each experiment, acid was cooled to 293 K, and its volume was measured. Using a standard hydrometer the density of the acid was measured followed by determination of the concentration of lookup tables (weight fraction monohydrate H<sub>2</sub>SO<sub>4</sub>) and recalculation on weight fraction of water.

The peculiarity of this concentrating process was the fact that during the acid heating to the temperature which corresponded to the boiling temperature of the initial concentration, the acid was boiled and then after some time due to increased concentration the boiling stopped and the concentrating mainly occurred during evaporation from the surface of the liquid phase. In that case, when the process was carried out below the boiling point of the starting acid or the heating temperature did not reach the boiling point (highly concentrated acid) the concentrating took place only during evaporation.

## 2.2. Data Processing

The data processing was carried as follows. The experimental results were presented in the form of



**Fig. 1.** The dependence of water weight fraction in the acid on the time of concentrating for different air flow rates (m/s):  $1.06 \cdot 10^{-3}$  (1);  $2.12 \cdot 10^{-3}$  (2);  $3.93 \cdot 10^{-3}$  (3);  $8.06 \cdot 10^{-3}$  (4) and  $10.6 \cdot 10^{-3}$  (5).  $t_a = 415$  K;  $t_g = 293$  K;  $x_0 = 0.4$

dependence of change in time (kinetic curves) of water weight fraction in the acid solution  $x = f(t)$  and the weight of the formed vapor  $Q = f(t)$ . Value  $Q$  was determined as the difference between the initial weight of acid and the weight of acid at a predetermined timing. As an example, such dependencies for different air flows are presented in Figs. 1 and 2, which indicate significant impact of air flow rate passing over the sulfuric acid surface on the process of its concentrating.

Similar studies of the influence of other process parameters have shown that the process is also significantly affected by acid heating temperature and its initial concentration but is relatively insignificantly affected by air temperature in the above range of its change.

The evaporation rate in this study is defined as:

$$w = \frac{1}{F} \cdot \frac{dQ}{dt} \quad (1)$$

where  $F$  – evaporation surface area.

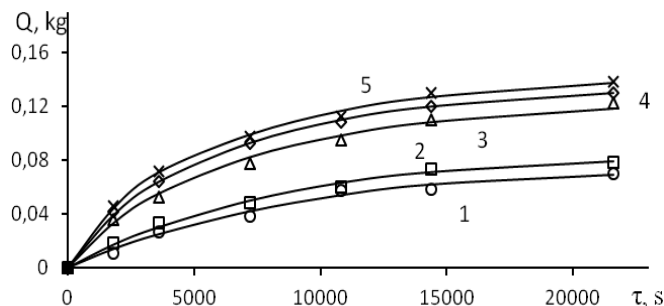
At the same time, due to a significant error of numerical differentiation, especially on the flat sections of the kinetic curves, initially the dependence  $Q = f(\tau)$  is approximated by a power function (2):

$$Q = At^n \quad (2)$$

where  $A$  and  $n$  – experimental coefficients. Then setting values of time, the evaporation rate is calculated by the formula:

$$w = \frac{An}{F} t^{n-1} \quad (3)$$

For the set values of time the value of  $x$  is determined from the experimental dependence  $x = f(t)$ . On the basis of obtained data the relation between the evaporation rate of components from acid solution and the weight fraction of water was established as a function  $w = f(x)$ .



**Fig. 2.** The dependence of vapor weight on the time of concentrating for different air flow rates (m/s):  $1.06 \cdot 10^{-3}$  (1);  $2.12 \cdot 10^{-3}$  (2);  $3.93 \cdot 10^{-3}$  (3);  $8.06 \cdot 10^{-3}$  (4) and  $10.6 \cdot 10^{-3}$  (5).  $t_a = 415$  K;  $t_g = 293$  K;  $x_0 = 0.4$

### 3. Results and Discussion

During analysis of experimental data, it was found that the dependence  $Q = f(\tau)$  in logarithmic coordinates is linearized with a kink at the line (Fig. 3). The time at which this kink is detected corresponds to a definite value of weight fraction of water in the acid solution ( $x_k$ ). In the case when the weight fraction of water in the acid solution at a predetermined time of concentrating exceeds the value  $x_k$ , for example, 60% acid ( $x_0 = 0.4$ ) at the temperature of 373 K (Fig. 3a), or a weight fraction of water in the initial acid is less than  $x_k$  (Fig. 3b), the line has no kink.

Such character of this dependence indicates a change in regularity of the evaporation acid at going through  $x_k$ . This can be explained by the fact that when  $x \geq x_k$ , mainly water evaporates as a more volatile component. If  $x < x_k$ , monohydrate  $H_2SO_4$  begins to influence evaporation. This is confirmed by the data [1], according to which at low acid concentration, the vapor above it contains practically no monohydrate  $H_2SO_4$  whereas its content increases sharply at high concentrations. Even at 80% acid ( $x_0 = 0.2$ ) only its traces are found in the vapor; at 90% acid it is about 10 % and at 98.3% the composition of the vapor and liquid phases is equal (azeotropic point). Thus, the change from one pattern of evaporation to another occurs when approaching  $x_k = 0.2$ .

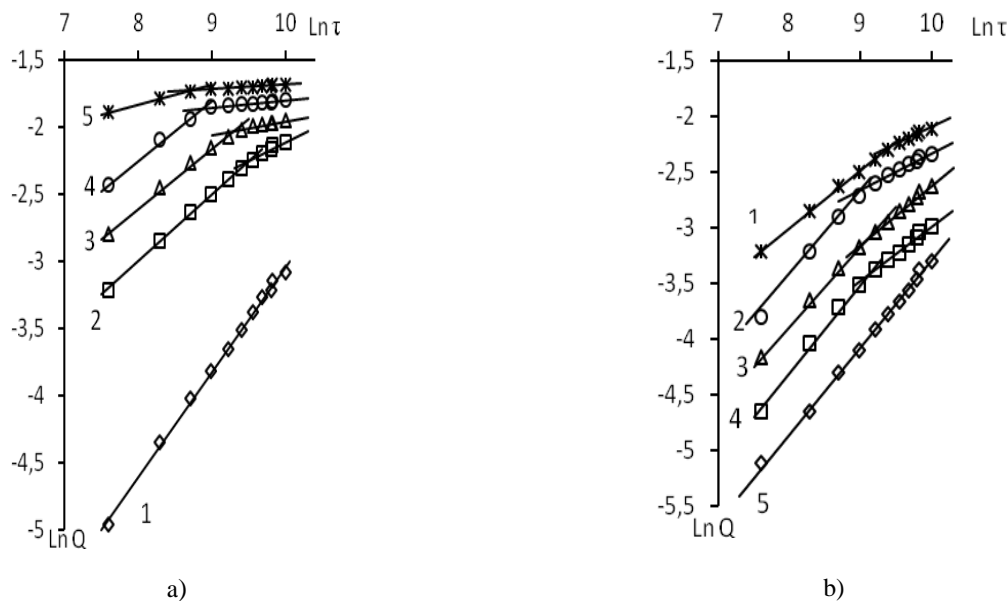
Values of  $x_k$  for different evaporation conditions of the acid are shown in the Table. They are determined by the position of kink lines on the graphs of kinetic dependences of evaporation. From these data, it follows that  $x_k$  is not a constant. Within this range of the process parameters the value of  $x_k$  is changed from 0.202 to 0.340 (acid concentration 66.0–79.8 %). Moreover, there is a tendency  $x_k$  offset toward lower values when the temperature of acid, air rate, and air temperature increases and the weight fraction of water in the acid decreases.

It is obvious that the dependence of  $w = f(x)$  in ranges of variation of the weight fraction of water in the acid solution at  $x \geq x_k$  and  $x < x_k$  must differ. As an example, Fig. 4 shows the graphs of depending for the range  $x \geq x_k$ , obtained at various temperatures of the acid. These graphs show that with the increase of weight fraction of water in the acid, evaporation rate increases, the curves are characterized by a sharp rise at greater values of  $x$ . The evaporation rate increases with increasing temperature of the acid. It was also found that it increases with increasing air rate, but the initial concentration and air temperature have little effect on the rate of evaporation of the acid.

Dependences  $w = f(x)$  in semi-log coordinates are straight (Fig. 4b), which allowed to approximate them by an exponential function:

$$w = w_0 e^{kx} \quad (4)$$

where  $w_0$  and  $k$  – the experimentally determined parameters, and if we take  $k \rightarrow 0$ , then  $w_0$  has the physical meaning of evaporation rate of monohydrate  $H_2SO_4$ .



**Fig. 3.** Dependence  $Q = f(\tau)$  in logarithmic coordinates for different temperatures of acid (a) and different initial mass fractions of water in the acid (b).

For (a):  $v = 3.93 \cdot 10^{-3}$  m/s;  $t_g = 293$  K;  $x_0 = 0.4$ ;  $t_k = 373$  K (1);  $t_k = 415$  K (2);  $t_k = 423$  K (3);  $t_k = 453$  K (4) and  $t_k = 473$  K (5)

For (b):  $v = 3.93 \cdot 10^{-3}$  m/s;  $t_g = 293$  K;  $t_k = 415$  K;  $x_0 = 0.4$  (1);  $x_0 = 0.35$  (2);  $x_0 = 0.3$  (3);  $x_0 = 0.25$  (4) and  $x_0 = 0.2$  (5)

Values of model parameters for different conditions of evaporation

Evaporation conditions				Model parameters				
$t_w$ , K	$v \cdot 10^3$ , m/s	$t_g$ , K	$x_0$	$x_k$	$x \geq x_k$		$x < x_k$	
					$k$	$w_0 \cdot 10^3$ , kg/m <sup>2</sup> ·s	$k$	$w_0 \cdot 10^3$ , kg/m <sup>2</sup> ·s
373	3.93	293	0.40	—	7.39	0.01672	—	—
415	3.93	293	0.40	0.275	7.52	0.09593	9.60	0.01648
423	3.93	293	0.40	0.200	7.02	0.1805	16.09	0.0175
453	3.93	293	0.40	0.170	7.24	0.2688	11.29	0.02006
473	3.93	293	0.40	0.202	7.01	0.3296	7.21	0.04296
415	1.06	293	0.40	0.340	10.96	0.009889	8.21	0.001630
415	2.12	293	0.40	0.315	9.56	0.02345	12.50	0.004966
415	3.93	293	0.40	0.275	7.52	0.09593	9.60	0.01648
415	8.06	293	0.40	0.265	5.81	0.2944	6.87	0.09462
415	10.6	293	0.40	0.240	3.94	0.8271	6.41	0.1213
415	3.93	293	0.40	0.275	7.52	0.09593	9.60	0.01648
415	3.93	415	0.40	0.245	6.96	0.1200	9.52	0.02564
415	3.93	473	0.40	0.240	6.15	0.1591	9.84	0.02207
415	3.93	293	0.40	0.275	7.52	0.09593	9.60	0.01648
415	3.93	293	0.35	0.244	5.60	0.1607	11.00	0.01765
415	3.93	293	0.30	0.254	7.06	0.0993	10.59	0.02304
415	3.93	293	0.25	0.212	8.97	0.0581	9.85	0.02554
415	3.93	293	0.20	—	—	—	9.87	0.03231

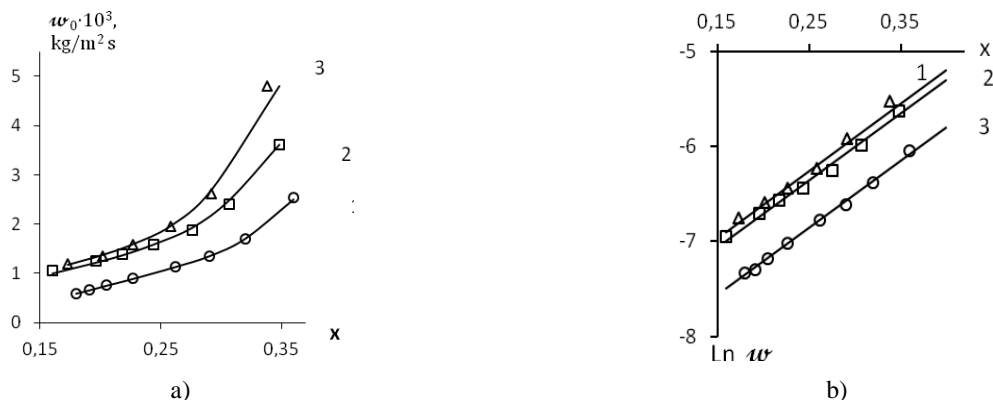


Fig. 4. Dependence of acid evaporation rate on the weight fraction of water in it if  $x \geq x_k$  in the physical coordinates (a) and semi-logarithmic coordinates (b). The values  $v = 3.93 \cdot 10^{-3}$  m/s;  $t_g = 293$  K;  $x_0 = 0.4$ ;  $t_k = 423$  K (1);  $t_k = 453$  K (2) and  $t_k = 473$  K (3)

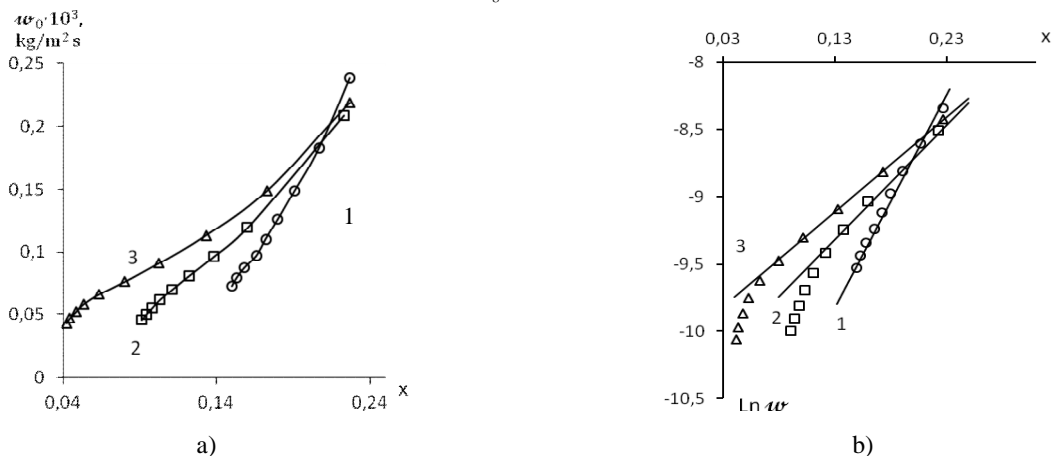


Fig. 5. The dependence of the acid evaporation rate on the weight fraction of water in it if  $x < x_k$  in the physical coordinates (a) and semi-logarithmic coordinates (b). The values  $v = 3.93 \cdot 10^{-3}$  m/s;  $t_g = 293$  K;  $x_0 = 0.4$ ;  $t_k = 423$  K (1);  $t_k = 453$  K (2) and  $t_k = 473$  K (3)

Fig. 5 shows the dependences  $w = f(x)$  in the range  $x < x_k$ . By their nature, they differ from the previous ones, and can also be approximated by an exponential function of the above form. However, when the value of the weight fraction of water in the acid is approaching an azeotropic point that takes place for a highly concentrated acid obtained, for example, at the temperature above 453 K, deviation of the experimental values from the exponential function is observed (curves 2 and 3 in Fig. 5b). This limits the use of this equation in the range  $x < x_k$ .

Table shows the experimentally determined parameters of the proposed model for the different conditions of evaporation. Analysis of the data shows that in each change range of the water weight fraction in the acid, parameters  $w_0$  and  $k$  have different values. Regardless of the range of variation of the water weight fraction in the acid solution, conditions of the process have relatively little effect on the value  $k$  except for the air rate in the range  $x \approx x_k$ . In this range, with increasing air rate parameter  $k$  is significantly reduced. The parameter  $w_0$  tends to increase with increasing temperature of the acid, temperature and velocity of the air. The initial weight fraction of water in the acid has little effect on this parameter.

## 4. Conclusions

The results of experimental researches have shown different character of evaporation of the components from the sulfuric acid solution into the air flow at high water content as well as at its content less than a certain critical value, when the monohydrate  $H_2SO_4$  begins to evaporate. The value of the critical water content of the acid depends on the operating parameters of the evaporation process.

The dependence of the evaporation rate of the components from the acid solution on its composition, which can be approximated by an exponential function well enough in the range of the water content greater than the critical, was established. For the range of water content less than critical there is a deviation of experimental data from this function. This deviation increases sharply when approaching the azeotropic point. The empirical equation based on the set function can be used at engineering calculations of low-temperature sulfuric acid concentrating process carried out in a flow of neutral gas (air).

## List of abbreviations

$C_0$  – the initial acid concentration (weight fraction monohydrate  $H_2SO_4$ ), %;

$Q$  – weight of the formed vapor, kg;

$t_a$  – acid temperature, K;

$t_g$  – the temperature at the inlet to the flask, K;

$v$  – flow rate at the evaporation surface area, m/s;

$w$  – the rate of acid solution evaporation, kg/m<sup>2</sup>·s;

$x$  – weight fraction of water in the acid solution;

$x_0$  – initial weight fraction of water in the acid solution;

$x_k$  – critical value of weight fraction of water in the acid solution;

$\tau$  – time, s;

$w_0$  – experimental parameter;

$k$  – experimental dimensionless parameter.

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## ШВИДКІСТЬ ВИПАРОВУВАННЯ КОМПОНЕНТІВ З РОЗЧИНУ СУЛЬФАТНОЇ КИСЛОТИ ЗА ЇЇ КОНЦЕНТРУВАННЯ У ПОТОЦІ ПОВІТРЯ

**Анотація.** Запропоновано методику експериментального визначення швидкості випаровування компонентів з розчину сульфатної кислоти за її концентруванні у потоці нейтрального газу. За допомогою цієї методики встановлена залежність швидкості випаровування від складу розчину кислоти. Виявлено критичне значення масової частки води у розчині, за якої змінюється характер цієї залежності. Отримано емпіричне рівняння для наближеного розрахунку швидкості випаровування компонентів з розчину кислоти в потік повітря.

**Ключові слова:** сульфатна кислота, концентрування, швидкість випаровування, нейтральний газ, моногідрат.