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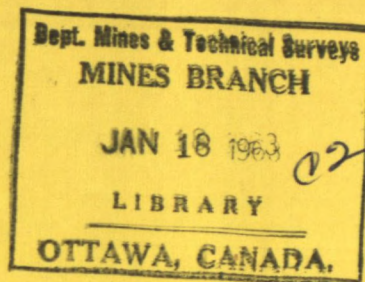
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KINETIC STUDIES OF THE
THERMAL DECOMPOSITION OF
FERRIC SULPHATE AND
ALUMINUM SULPHATE

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EXTRACTION METALLURGY DIVISION

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Kinetic Studies of the Thermal Decomposition of Ferric Sulphate and Aluminum Sulphate

N. A. WARNER² and T. R. INGRAHAM³

Kinetic studies were made of the thermal decompositions of ferric sulphate and aluminum sulphate. The reaction product gases were swept from the samples. Cylindrical pellets prepared from chemically pure anhydrous powders were used, and mathematical corrections were made to relate the reaction rate to the area of the interface between the undecomposed sulphate and the oxide product. The interface is the local of the reaction. The rate of the decomposition reaction is proportional to the area of this interface. Studies on ferric sulphate have shown that the rate of decomposition is also directly proportional to the difference between the equilibrium pressure of sulphur dioxide (or oxygen) over the sample and the partial pressure of sulphur dioxide (or oxygen) in the gas stream. The activation energies are 19.9 kcal. and 64.0 kcal. respectively for the ferric sulphate and aluminum sulphate decompositions. No oxysulphates were detected as intermediates in the transition from the normal sulphates to the oxides.

On a étudié la cinétique de la décomposition thermique du sulphate ferrique et du sulphate d'aluminium. On a débarrassé les échantillons des produits gazeux de réaction. Les auteurs ont préparé pastilles cylindriques à partir de poudres anhydres chimiquement pures. Ils ont fait des corrections mathématiques pour relier la vitesse de réaction à l'aire interfaciale entre le sulphate non décomposé et le produit oxydé. L'interface étant le site de la réaction, la vitesse de décomposition est proportionnelle à l'aire de l'interface. Les études sur le sulphate ferrique ont montré que la vitesse de décomposition est aussi directement proportionnelle à la différence entre la pression d'équilibre de l'anhydride sulphureux (ou de l'oxygène) au-dessus de l'échantillon et la pression partielle de l'anhydride sulphureux (ou de l'oxygène) dans le courant gazeux. Les énergies d'activation pour la décomposition du sulphate ferrique et du sulphate d'aluminium sont de 19.1 kcal. et 64.0 kcal. respectivement. Les auteurs n'ont pas décelé d'oxysulphates comme produits intermédiaires lors du passage des sulphates normaux en oxydes.

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In a previous publication by the authors⁽¹⁾, work was reported on experiments done to assess the possibility of making a selective separation of ferric sulphate and aluminum sulphate by the method of thermal decomposition and leaching proposed by Willard and Fowler⁽²⁾. From the experiments, which were

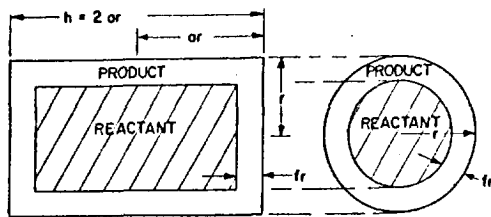


Figure 1—Diagram of the geometric changes which accompany the decomposition of a cylindrical pellet of $M_2(SO_4)_a$.

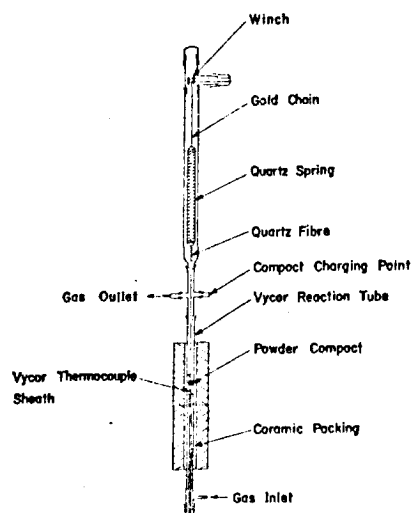


Figure 2—Diagram of the apparatus used in the decomposition studies.

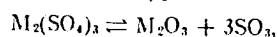
done by measuring the gas pressures developed by the dissociation of the sulphates, it was evident that aluminum sulphate was substantially more stable than ferric sulphate.

During the investigation, it was found that no information was available on the relative rates of decomposition of the two compounds. Since this information would be important in any practical application of the methods proposed by Willard and Fowler⁽²⁾, it was decided to make a study of the kinetics of thermal decomposition of the two compounds. Because pure anhydrous ferric sulphate and aluminum sulphate are not readily available as coarse crystals, it was decided to make the experiments with the finely divided powders that remain after the removal of water from the chemically pure hydrates.

Kinetic studies on powdered materials can be quite difficult because for those reactions which obey the linear rate law, which states that the rate is controlled by the amount of surface area exposed, the observed rate of reaction for each particle is inversely proportional to the radius of the particle⁽³⁾. To avoid the problems associated with particles of a variety of sizes, the technique used by Peretti⁽⁴⁾ was adopted. In his study of the oxidation of cupric sulphide, Peretti⁽⁴⁾ used samples of cupric sulphide prepared by compressing finely divided, chemically pure cupric sulphide into a dense cylindrical pellet. When the pellets were examined at various intervals during the roasting, Peretti⁽⁴⁾ observed, in accordance with the prediction of Langmuir⁽⁵⁾, that the interface between the solid phases was the local of the reaction. He also observed that the rate of penetration of the interface into the body of the pellet was almost constant.

On the basis of Peretti's⁽⁴⁾ observation, it thus seemed reasonable to expect that this study of the rates of decomposition of ferric sulphate and aluminum sulphate could be made on pellets from finely divided powders, and that the linear rate law, which is often applicable to individual solid particles, might also be applied to a tightly compacted agglomerate of particles.

Because there is a substantial loss in weight accompanying a thermal decomposition of the type



it was decided to suspend the powder compacts of ferric sulphate and aluminum sulphate on a quartz spring, and to follow the progress of the reaction by periodic observation of the weight loss. The fraction of decomposition, α , would be calculated from the ratio of the weight lost after time t , to the weight lost at the end of the reaction.

Theory

The linear rate law in its integrated form is:

$$x = vt.$$

In this equation, v is the velocity of migration of an interface, expressed in terms of a linear dimension x and a time t . This form of the equation implies a constant area of the interface. When the area of the interface changes as the reaction proceeds, it is necessary to introduce a factor f , which represents the fractional change in the linear dimension x with a change in the fraction α of material reacted. Thus,

$$xf = vt \dots \dots \dots (1)$$

The factor f may have various forms, depending on the shape of the particle to which the calculation is applied. For example, the expression

$$r[1 - (1 - \alpha)^{1/3}] = vt \dots \dots \dots (2)$$

was used by Spencer and Topley⁽³⁾ to describe the velocity of migration of the silver carbonate-silver oxide interface for small spherical particles of silver carbonate. In this application, the linear dimension x is the radius, r , of the spherical pellet and the quantity

$$1 - (1 - \alpha)^{1/3}$$

represents the value of f applicable to a spherical pellet.

Equation (2) was modified slightly by McKewan^(6,7,8) and used to describe the kinetics of reduction of iron oxide pellets:

$$rd[1 - (1 - \alpha)^{1/3}] = kt \dots \dots \dots (3)$$

In this modification, McKewan^(6,7,8) incorporated the density, d , of the pellet into the equation to permit expression of the reaction rate constant, k , as the weight of reactant decomposing per unit time per unit of interfacial area. The inclusion of d in the equation is particularly useful in studies involving powder compacts, because it permits correlation of the results obtained from experiments with pellets of different densities.

Although the equality,

$$f = 1 - (1 - \alpha)^{1/3}$$

was rigorously derived only for spheres, it is applicable to cubes and to cylindrical pellets having approximately spherical proportions. For cylindrical pellets having other proportions, it is necessary to derive a more exact expression. This can be done by designating the dimensions of the pellet as shown in Figure 1, where a is used to express the ratio of the height to the diameter of the pellet.

From the pellet dimensions shown in Figure 1, it is evident that the fraction of material decomposed, α , can be expressed as:

$$\alpha = \frac{\text{original volume} - \text{unreacted volume}}{\text{original volume}}$$

$$\alpha = \frac{2a\pi r^3 - 2(ar - fr)\pi(r - fr)^2}{2a\pi r^3}$$

$$\alpha = 1 - \left(\frac{a - f}{a}\right)^3 \dots \dots \dots (4)$$

When the pellet height and diameter are equal, the pellet approaches a spherical form and $a = 1$.

Hence

$$\alpha = 1 - (1 - f)^3 \text{ or } f = 1 - (1 - \alpha)^{1/3}$$

Equation (4) is cubic and it can be solved for f most readily by a graphic method. This is done by first calculating various

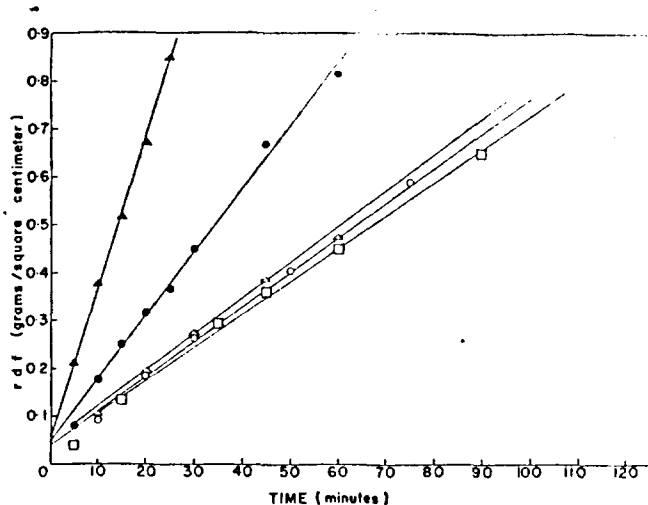


Figure 3—Rate of decomposition of ferric sulphate expressed as a weight change per unit area of sulphate-oxide interface.

	T(°K)	d(g/cm ³)	a
▲	1123	1.571	1.062
●	1023	1.583	0.969
△	973	1.547	0.674
○	973	1.471	1.086
□	973	1.566	1.520

values of a from assumed values of f between 0.1 and 0.8. The values of a and f are then plotted to form a graph, and the graph is used to obtain the value of f corresponding to each experimental value of a . The value of f so obtained is then substituted, together with the pellet density and the pellet radius, in Equation (3) to obtain k , the linear rate constant expressed as the weight of reactant decomposed per unit time per unit of interface area.

The Preparation of Materials

Aluminum sulphate and ferric sulphate, both of reagent grade, were dehydrated by heating to constant weight at a temperature of about 400°C. The dehydrated powders were compressed into pellets of different heights but of a constant diameter of 1.29 cm. To facilitate suspending the pellets in the apparatus, a small platinum wire was embedded in the centre of each pellet during the pressing operation. The wire was bent to form a hook for attaching the pellet to the quartz spring in the apparatus.

Apparatus and Procedure

The apparatus used in the experiments is shown in Figure 2. The pellet was suspended from a quartz spring attached by a gold chain to a winch. The winch was used to adjust the position of the top of the spring so as to keep the pellet in the same position in the furnace as decomposition proceeded. The weight loss of the pellet was determined from the spring extension as read with a cathetometer.

The nitrogen stream, which was used in the first group of experiments to sweep the liberated sulphur trioxide from the pellet, was preheated in ceramic packing. In the second group of experiments, in which a sweep gas consisting of sulphur trioxide, sulphur dioxide, oxygen and nitrogen was used, a platinized asbestos catalyst was substituted for a portion of the ceramic packing, to ensure that the gases were present in equilibrium proportions.

The temperature of the pellet was assumed to be the temperature of the surroundings. Experiments in which this temperature was compared with the temperature in the interior of the pellet had shown the assumption to be a valid one, except when the decomposition reactions were very rapid at high temperatures.

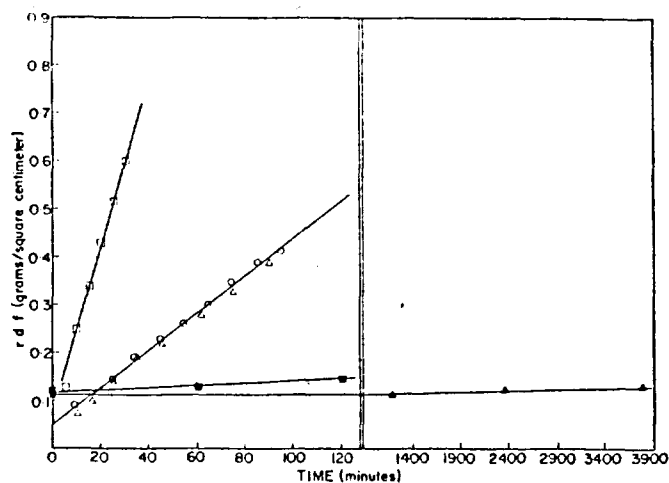


Figure 4—Rate of decomposition of aluminum sulphate expressed as a weight change per unit area of sulphate-oxide interface.

	T(°K)	d(g/cm ³)	a
□	1223	1.144	1.318
○	1123	1.459	1.155
△	1123	1.584	1.016
■*	1023	1.445	1.178
▲*	923	1.445	1.148

*partly decomposed

When the reaction was rapid, the temperature within the pellet was sometimes observed to lag 50°C. behind the temperature of the area surrounding it. This effect was expected from an endothermic reaction, and to prevent it from influencing the results, the decompositions were done slowly.

The procedure used in making a run was as follows: After the material had been compressed to form a pellet, the pellet was weighed and its dimensions were measured and used to calculate its density. The pellet was then hung on the quartz spring, which had been retracted into the cool zone of the apparatus. After a steady temperature had been attained in the furnace, the pellet was lowered into the reaction area and readings of the decreasing spring extension were made during the decomposition. Periodically, the top of the spring was lowered to maintain a constant position of the pellet in the furnace.

Results and Discussion

The results obtained from experiments in which a preheated stream of nitrogen was passed over pellets of ferric sulphate and aluminum sulphate are shown in Figures 3 and 4. In the experiments, a nitrogen flow rate of about 500 ml./min. was used. At this flow rate, the rate of the decomposition reaction is independent of the flow rate. The linearity of the lines in Figures 3 and 4 support the conclusion that both decomposition reactions, when done in a sweep of nitrogen gas, are properly described by the linear rate law. It is also reasonable to conclude that since variations in the thickness of the product layer do not appear to influence the rate of the reaction, then the product layer must be quite porous.

To obtain activation energies for the reactions, the logarithm of the rate constant, k_a (slope of each line in Figures 3 and 4) was plotted against its corresponding reciprocal temperature. This graph is shown in Figure 5. Each line was fitted by the method of least squares, and from the equations of the lines, the following expressions were obtained for the linear reaction rate constants. For ferric sulphate:

$$k_a = 2.25 \times 10^2 \exp(-19,900/RT).$$

For aluminum sulphate:

$$k_a = 1.14 \times 10^{10} \exp(-64,000/RT).$$

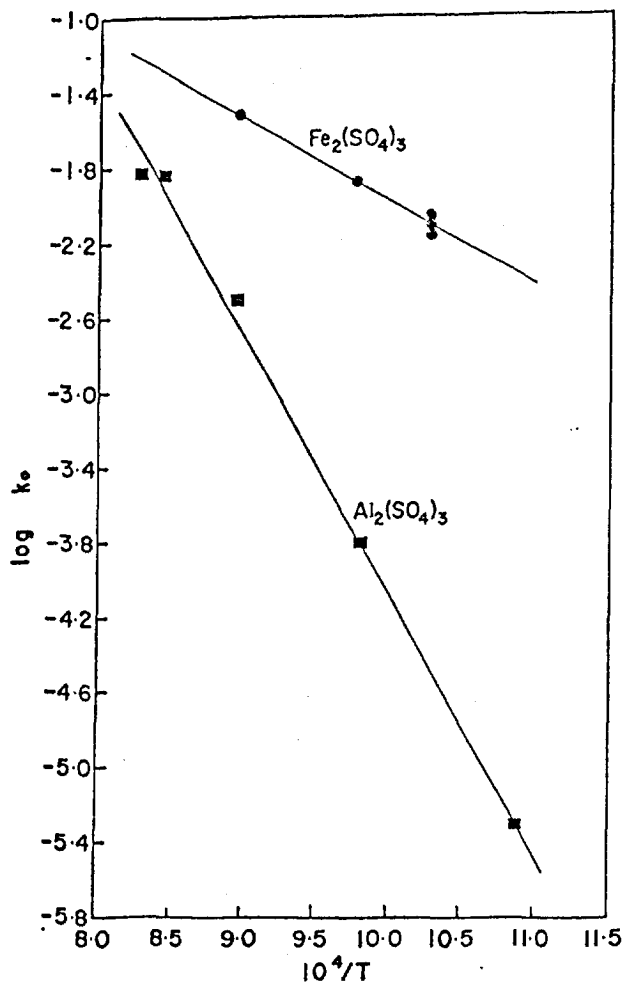


Figure 5—Arrhenius relationships for ferric sulphate and aluminum sulphate.

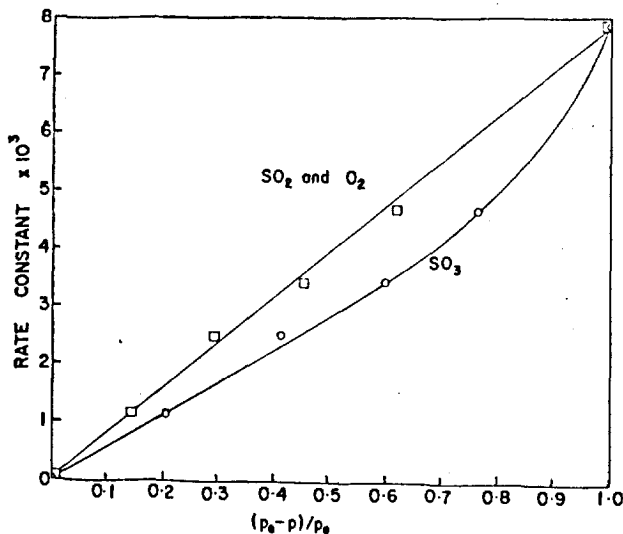
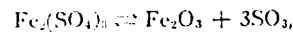


Figure 6—Variation in the rate of decomposition of ferric sulphate with fractional driving force.

In these expressions, the rate constant has been designated as k_0 to indicate that no sulphur trioxide, sulphur dioxide or oxygen was introduced into the stream of nitrogen gas used to sweep the sample. The quantities 19,900 and 64,000 are the activation energies in calories per mole for the ferric sulphate and the aluminum sulphate decompositions respectively and the quantities 2.26×10^2 and 1.14×10^{10} are the frequency factors, expressed

in the units of grams per square centimetre of surface area per minute.

It is of interest to compare the activation energy for the ferric sulphate decomposition reaction with the free energy change computed for the reaction by the authors⁽⁹⁾. It was shown that the free energy relationship for the reaction



is

$$\Delta G = 125,840 - 119.75T \dots \dots \dots (5)$$

In this expression, the large entropy term of 119.7 cal./mole/deg. results in part from the expulsion of three molecules of sulphur trioxide from the highly ordered state in the solid to the random state in the gas phase. Although the heat of reaction is 125.8 kcal./mole at 1,000°K, because of the large entropy change, the change in free energy for the decomposition reaction is only about 6 kcal./mole. Since the activation energy for the decomposition reaction is about 20 kcal./mole, it is evident that the activation energy for the recombination reaction should be about 14 kcal./mole. No attempts have been made to measure this activation energy, but such a small activation energy should be acquired easily, especially because a substantial release of heat might be expected to result from adsorption on ferric oxide. The fact that the reverse reaction does not proceed readily in practice, may be interpreted as indicating that ferric sulphate forms a protective coating on the ferric oxide and the rate of formation of additional ferric sulphate is controlled by the rate of transfer of the reactant(s) across the ferric sulphate layer. Experiments done by Alecock⁽⁹⁾ on the sulphation of cobalt oxide support this conclusion.

In the second group of experiments, a study was made of the effect of sulphur trioxide, sulphur dioxide and oxygen pressures on the rate of the ferric sulphate decomposition reaction. This was done by passing various mixtures of sulphur dioxide, oxygen and nitrogen through the ceramic pre-heating unit, where, by the action of a platinum catalyst supported on asbestos, equilibrium amounts of sulphur trioxide, sulphur dioxide and oxygen were formed. All of the experiments were done at a temperature of 700°C. and a total pressure of one atmosphere. The initial and equilibrium gas compositions are shown in Table 1. The equilibrium gas compositions were calculated by the method of successive approximation suggested by Kellogg⁽¹⁰⁾.

TABLE I
DECOMPOSITION RATE AS A FUNCTION OF GAS COMPOSITION
 p_r for $\text{SO}_3 = 0.0794$; p_r for $\text{SO}_2 = 0.128$; p_r for $\text{O}_2 = 0.064$

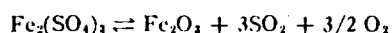
Initial Composition at room temperature (atm)			Rate Constant $k \times 10^3$	Equilibrium Composition at 700°C. (atm)		
p_{SO_3}	p_{O_2}	p_{N_2}		p_{SO_3}	p_{SO_2}	p_{O_2}
0.000	0.000	1.000	7.92	0.0000	0.0000	0.0000
0.067	0.033	0.900	4.71	0.0186	0.0486	0.0243
0.100	0.050	0.850	3.46	0.0320	0.0696	0.0348
0.134	0.066	0.800	2.54	0.0467	0.0897	0.0449
0.167	0.083	0.750	1.15	0.0632	0.109	0.0544
0.200	0.100	0.700	> 0	0.0800	0.128	0.0640

The effect of the presence of carbon dioxide on the rate of decomposition of calcium carbonate has been studied by Zawadski and Bretsznajder⁽¹¹⁾, who showed that the rate of the reaction is directly proportional to the driving force. The driving force was defined as the difference between the equilibrium pressure of carbon dioxide over the sample and the pressure of carbon dioxide maintained in the system.

To test the application of this relationship to the reaction for the decomposition of ferric sulphate, the driving force for

the reaction was calculated for sulphur trioxide, sulphur dioxide and oxygen by subtracting the partial pressures of each gas, shown in Table 1, from the equilibrium pressure of that gas over the sample at 700°C. The equilibrium pressures were calculated from the free energy relationship shown in Equation (5) and the data of Evans and Wagman⁽¹²⁾ for the decomposition of sulphur trioxide. The results are shown as a function of the fractional driving force $(p_e - p)/p_e$ in Figure 6.

From Figure 6 it is evident that the relationship between the rate of reaction and the fractional driving force is linear for both sulphur dioxide and oxygen, but curved for sulphur trioxide. Even though there are not sufficient data to specify the reaction mechanism, there is an indication, because of the linearity of the sulphur dioxide-oxygen curve, that these constituents may be more directly concerned than sulphur trioxide in the reaction mechanism. If this were true, it would be preferable to represent the decomposition reaction as:



The free energy change for this reaction, as computed from the data of the authors⁽¹⁾ is:

$$\Delta G = 194,165 - 184.55T.$$

From recent experimental work⁽⁹⁾, there has been an indication that an oxysulphate of iron may be formed during the decomposition of ferric sulphate, but no evidence has been found in this work for the existence of such an intermediate compound.

By combining the equations relating the effects of particle geometry, frequency factor and activation energy, with the equations for the effects of change in rate due to changes in the partial pressure of either sulphur dioxide or oxygen, the following general expression has been developed for calculating the fractional amount of decomposition α , obtained after a reaction period of t minutes, for an approximately spherical pellet of ferric sulphate:

$$rd[1 - (1 - \alpha)^{1/3}] = 2.26 \times 10^2 \exp(-19,900/RT) [(p_e - p)/p_e] t$$

Conclusions

Experiments done on the rates of thermal decomposition of ferric sulphate and aluminum sulphate have shown that it is possible to make kinetic studies using finely divided powders, by compressing the powders into a cylindrical form and making

mathematical corrections for the change in interfacial area which results as the reaction proceeds. It has been shown that the rate of decomposition of ferric sulphate is much more rapid than that of aluminum sulphate. Because of the large difference in the activation energies of the reactions, the difference in the rates of reaction is greatest at the lower temperatures. It has also been shown that the rate of decomposition of ferric sulphate varies with the driving force, when the driving force is defined as the difference between the equilibrium pressure of sulphur dioxide over the sample and the partial pressure of sulphur dioxide in the sweeping gas. The same relationship is applicable to the partial pressure of oxygen, but this relationship does not hold for the sulphur trioxide constituent of the gas.

Acknowledgements

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References

- (1) Warner, N. A. and Ingraham, T. R., *Can. J. Chem.* **38**, 2196 (1960).
- (2) Willard, H. H. and Fowler, R. D., *J. Am. Chem. Soc.* **54**, 496 (1932).
- (3) Spencer, W. D. and Topley, B., *J. Chem. Soc.*, 2633 (1929).
- (4) Peretti, E. A., *Discussions Faraday Soc.* **4**, 174 (1948).
- (5) Langmuir, I., *J. Am. Chem. Soc.* **38**, 2263 (1916).
- (6) McKewan, W. M., *Trans. Am. Inst. Mining Met. Engrs.* **212**, 791 (1958).
- (7) McKewan, W. M., *Trans. Am. Inst. Mining Met. Engrs.* **218**, 2 (1960).
- (8) McKewan, W. M., *Trans. Am. Inst. Mining Met. Engrs.* **221**, 140 (1961).
- (9) Alcock, C. B., Royal School of Mines, London. Private communication.
- (10) Kellogg, H. H., *Trans. Am. Inst. Mining Met. Engrs.* **206**, 1105 (1956).
- (11) Zawadski, J. and Bretsznajder, S., *Trans. Faraday Soc.* **34**, 951 (1938).
- (12) Evans, W. H. and Wagman, D. D., *Nat. Bur. Standards (J. Research)* **49**, 141 (1952).

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