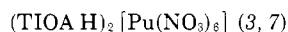
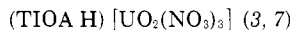
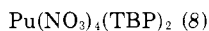
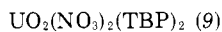


ORGANIC SOLVENTS

The diffusion coefficients of U and Pu in some organic solvent systems, previously equilibrated with aqueous HNO₃ solutions, are listed in Tables I and II. The HNO₃ equilibrium concentration of the organic phase is noted in the second column. The complexes formed in the organic phase are well defined:



They are undissociated and considerably larger than the ionic species in the aqueous phase and possess smaller diffusion coefficients at a given temperature.

The activation energy for the diffusion of the uranium-TIOA complex (total U concentration $1 \times 10^{-5}M$) in 10% and 20% TIOA/xylene is 2.35 ± 0.06 kcal./mole and 2.35 ± 0.02 kcal./mole, respectively.

Table I. Diffusion Coefficients of U in TBP and TIOA

Org. Phase	HNO _{3,org} [M]	Uranium [M], Total	Temp., °C.	D _U × 10 ⁶ , Cm. ² Sec. ⁻¹
20% TBP-	0.002	1 × 10 ⁻⁵	25	3.98 ± 0.07
	0.033	1 × 10 ⁻⁵	25	4.17 ± 0.06
	0.290	1 × 10 ⁻⁵	25	4.32 ± 0.06
kerosine	0.033	0.5	25	2.27 ± 0.05
	0.29	0.5	25	1.88 ± 0.05
	...	1 × 10 ⁻⁵	25	3.88 ± 0.06
10% TIOA-	...	1 × 10 ⁻⁵	40	4.70 ± 0.06
	...	1 × 10 ⁻⁵	60	5.90 ± 0.08
20% TIOA-	...	1 × 10 ⁻⁵	25	3.05 ± 0.08
	...	1 × 10 ⁻⁵	40	3.71 ± 0.08
xylene	...	1 × 10 ⁻⁵	60	4.61 ± 0.09

^a Mean of three runs.

Table II. Diffusion of Pu(IV) tracer (10⁻⁴M) in TBP and TIOA

Org. Phase	HNO _{3,org} M	Temp., °C.	D _{Pu} × 10 ⁶ Cm. ² Sec. ⁻¹ ^a
20% TBP-	0.002	25	1.86 ± 0.05
	0.033	25	1.79 ± 0.05
kerosine	0.29	25	1.95 ± 0.05
	0.4	25	0.76 ± 0.03
10% TIOA-	0.4	35	1.56 ± 0.05
	0.4	45	2.96 ± 0.08
20% TIOA-	0.8	25	0.40 ± 0.03
	0.8	35	0.79 ± 0.04
xylene	0.8	45	1.50 ± 0.05

^a Mean of two runs.

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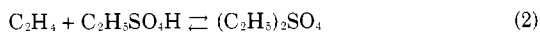
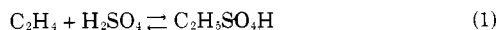
RECEIVED for review May 31, 1963. Accepted September 16, 1963.

Kinetics of the Reaction of Ethylene with Sulfuric Acid

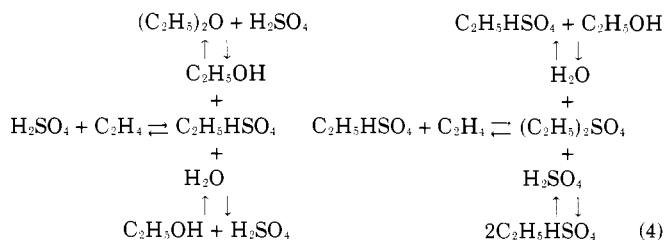
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AMONG THE EXAMPLES of complex chemical reactions that have widespread application are the reactions of olefins with sulfuric acid. The ethylene reactions with concentrated sulfuric acid actually involve a family of reactions of which the following are well known:



If ethylene is reacted with dilute sulfuric acid, reactions other than 1, 2, and 3 occur to some degree and the following equilibria are set up:



A kinetic study was made of the reactions in the ethylene-sulfuric acid-ethyl hydrogen sulfate-diethyl sulfate system. Concentration vs. time data were obtained for the reaction of concentrated sulfuric acid and diethyl sulfate to yield ethyl hydrogen sulfate, and these data were analyzed statistically to determine the most suitable kinetic model. The rate constants for this model were found to be highly dependent on the initial acid concentration. The suggested controlling reaction mechanism is the formation of a carbonium ion and its reaction with bisulfate or ethyl sulfate ions.

Reactions 1 and 2, with subsequent hydrolysis of the reaction products, according to the reactions given in 4, have particular industrial importance. Because the quantitative kinetic aspects of this system have not yet been thoroughly investigated in spite of its long-time record of industrial usage, information concerning the kinetic models and values of the corresponding rate constants is of both theoretical and practical interest.

Suter (11) and Ellis (6) give reviews of the ethylene-sulfuric acid system reactions and important related reactions, such as the acid-ester hydrolysis and ether formation.

The dissociation of ethyl hydrogen sulfate into diethyl sulfate (DES) and sulfuric acid, Reaction 3, is a homogeneous reaction, and the investigation of its kinetics is not subject to the same difficulties as those of heterogeneous Reactions 1 and 2. Some rate data are available (9) for this reaction which are discussed more fully later.

THEORETICAL CONSIDERATIONS

If Reaction 3 is second order in both the forward and reverse directions in the manner indicated by the stoichiometry, a possible expression for the rate of reaction is

$$-\frac{d(a_{C_2H_5SO_3H})}{dt} = k'_F(a_{C_2H_5SO_3H})^2 - k'_R(a_{(C_2H_5)_2SO})(a_{H_2SO_4}) \quad (5)$$

However, the proper reaction mechanism cannot be deduced from only a knowledge of the overall chemical reaction or stoichiometric equation. The true reaction mechanism may in fact involve species (atoms, ions, or radicals) which are not present in the overall observed reaction components. The usual technique is to carry out rate measurements by determining constituent concentrations as functions of time during the course of the reaction, and then from these kinetic data to determine a valid kinetic model. The kinetic model so determined is useful for practical calculations and predictions and has further value in that it may shed light on the real reaction mechanism. This was the procedure followed in this study.

If Reaction 3 is carried out at essentially constant volume, if its rate is given by Equation 5, if the activities are taken to be unity at unit mole fraction, and if (because of the lack of a suitable method of determining the activity coefficients of the reaction components) the tacit assumption is made that the activity coefficient products are constant, Equation 5 is transformed into

$$-\frac{dC_{C_2H_5SO_3H}}{dt} = k_F(C_{C_2H_5SO_3H})^2 - k_R(C_{(C_2H_5)_2SO})(C_{H_2SO_4}) \quad (6)$$

Similar expressions are readily developed for any kinetic model found applicable, and the above expressions have been given in detail only to illustrate the nature of the assumptions made. The effect of the assumption of constant activity coefficients was to throw all variations in the model not specifically taken into account by the concentration terms into the rate constants.

Since when ethylene is absorbed in dilute H_2SO_4 , several interrelated reactions are involved as shown in Equation 4, in order to simplify this study, concentrated (99.8 wt. %) sulfuric acid was used, thus eliminating all but Reactions 1, 2, and 3 from the complex Equilibria 4.

Reactions 1 and 2 above have been reported to be reversible reactions and are shown as such; this indicated that any study of Reaction 3 would be complicated by the simultaneous decomposition of diethyl sulfate and ethyl hydrogen sulfate, and thus Reaction 3 could not be followed independently. Such was not the case. It was found that upon mixing diethyl sulfate and sulfuric acid, the reverse reaction to ethyl hydrogen sulfate proceeded without evolution of ethylene. This finding was supported by the report (10) that a similar reaction of propylene with H_2SO_4 , though reversible, has its equilibrium far to the right, and by the fact that diethyl sulfate is a stable compound, indicating an extremely slow reverse reaction. Our finding was demonstrated qualitatively by evacuating a mixture of 99.8 wt. % sulfuric acid and diethyl sulfate, and noting the absence of a pressure change over several days. Consequently, it was possible to follow Reaction 3 separately from Reactions 1 and 2, and thus effect considerable simplification in the experimental procedure and data analysis. Since pure ethyl hydrogen sulfate is not available due to its spontaneous decomposition into sulfuric acid and diethyl sulfate, Reaction 3 had to be followed in the reverse direction.

EXPERIMENTAL

Practical grade diethyl sulfate obtained from the Eastman Organic Chemicals Co. was washed, neutralized, and dried. Sulfuric acid was prepared by mixing 96% analytical grade H_2SO_4 and fuming H_2SO_4 . Various reaction mixtures ranging from 29 to 67 mole per cent diethyl sulfate were quickly mixed and thermostated. Because mixtures high in initial H_2SO_4 concentration reacted much more rapidly than did those with high initial diethyl sulfate concentration, H_2SO_4 was always added to the diethyl sulfate to diminish the extent of the reaction until complete H_2SO_4 addition had been effected.

The bath temperature was maintained at $30.00 \pm 0.02^\circ C$. Approximately 15 seconds before the reaction mixture was to be sampled, the correct portion (0.2 to 0.5 ml.) was withdrawn through a rubber serum cap with a hypodermic syringe. At the proper time, the reaction was quenched by injecting the sample into a separatory funnel containing distilled water and bromoform. Analysis of each sample for the moles of each component of the reaction mix was carried out as described by Harris and Himmelblau (8). Additional details of the procedure can be found in (7) as well as the detailed experimental data and results.

RESULTS AND ANALYSIS

Figure 1 illustrates a set of typical results; two independent runs, 1a, and 1b, with almost identical starting compositions have been amalgamated to make up Figure 1. Reproducibility of the "a" reaction mixture data by that of the "b" mixture was good. To obtain a measure of the precision of the analytical procedure, reaction mixture 4b, while at equilibrium, was sampled twice at the same time for four different times. The confidence limits of these eight samples expressed as a percentage of the mean (for a 95% confidence level) were:

Diethyl sulfate	$\pm 0.8\%$
Sulfuric acid	$\pm 2.1\%$
Ethyl hydrogen sulfate	$\pm 1.5\%$

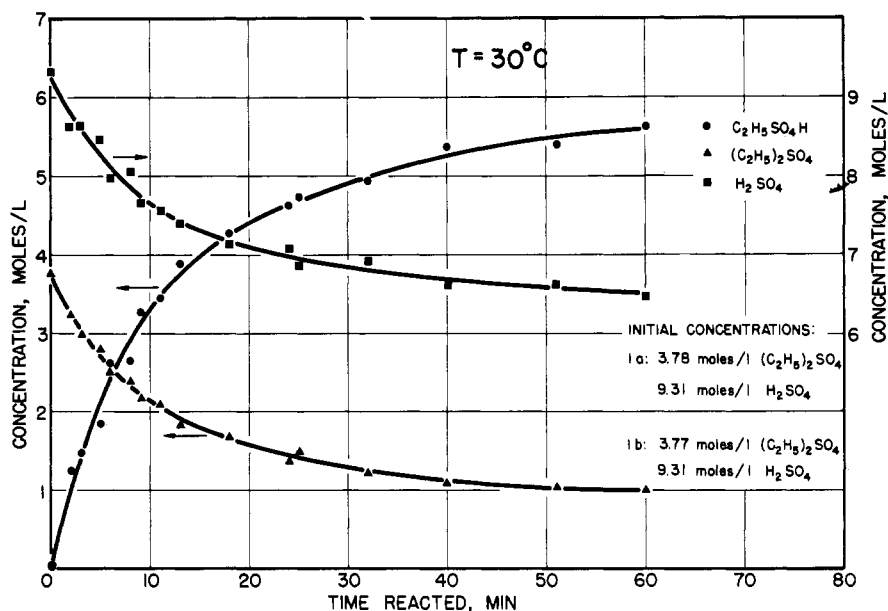


Figure 1. Concentrations as functions of reaction time-reaction mixtures 1a and 1b.

Rather than express the kinetic models in terms of one variable through the use of material balances (a procedure often found to give good results for one component and dismal results for the others), a statistical procedure similar to that of Box (2, 3, 4) was employed.

This method required that the concentration of each constituent in the reaction be known for various values of time, and that the model be linear with respect to the constants, or parameters, being determined, as is the case for many kinetic models. The rate of change of each component (x_i) in a general reaction system can be expressed by a set of first order differential equations

$$(dx_i/dt) = f_i(k_1, \dots, k_q, \dots, k_p, x_1, \dots, x_i, \dots, x_M), \quad (7)$$

where the functional form of f_i is determined by the selected kinetic model, P is the number of kinetic constants, and M is the number of components. Now for each differential Equation 7, a squared correlation coefficient, r_i^2 , can be defined, such that:

$$r_i^2 = 1 - \frac{\sum_{j=1}^N (y_{ij} - \hat{y}_{ij})^2}{\sum_{j=1}^N (y_{ij} - \bar{y}_i)^2} \quad (8)$$

where

$$\begin{aligned} y_{ij} &= \text{experimental value of } (dx_i/dt) \text{ measured at time } t_j \\ \hat{y}_{ij} &= f_i(k_1, \dots, k_q, \dots, k_p, x_{1j}, \dots, x_{ij}, \dots, x_{Mj}) \\ &= \text{predicted value of } (dx_i/dt) \text{ at time } t_j \\ \bar{y}_i &= \frac{1}{N} \sum_{j=1}^N y_{ij} \\ N &= \text{number of sets of observations} \end{aligned}$$

As can be seen from its formulation, the squared correlation coefficient, r_i^2 , is a measure of how well the rate of change of the i^{th} component concentration is expressed by the kinetic model for given values of the kinetic constants, k_q . For data which are well represented by the proposed kinetic model the term subtracted from 1 in Equation 8 will be small and the correlation coefficient will be close to unity; a perfect fit would require that $r_i^2 = 1$. Given any particular kinetic model, a set of constants, and a set of data, correlation coefficients are calculable for each dependent variable. The criterion which was used in this study to obtain the "best" constants for a particular model was to maximize the sum of the squared correlation coefficients, S , as given by

$$S = M - \left[\frac{\sum (y_{ij} - \hat{y}_{ij})^2}{\sum (y_{ij} - \bar{y}_i)^2} \right] - \dots - \left[\frac{\sum (y_{Mj} - \hat{y}_{Mj})^2}{\sum (y_{Mj} - \bar{y}_M)^2} \right] \quad (9)$$

Now for a given kinetic model and a particular set of data, S can be considered only a function of the constants, k_q . In order to determine the maximum value of S for all possible values of the constants it is convenient to partially differentiate S with respect to each constant, k_q , and set each partial derivative equal to zero, i.e.,

$$\frac{\partial S}{\partial k_q} = + \frac{\sum_{i=1}^M \sum_{j=1}^N 2(y_{ij} - \hat{y}_{ij})(\partial \hat{y}_{ij} / \partial k_q)}{Q_i} = 0 \quad (10)$$

where q ranges from 1 to P , and where

$$\begin{aligned} (\partial \hat{y}_{ij} / \partial k_q) &= \text{a function without any parameters} \\ Q_i &= \sum_{j=1}^N (y_{ij} - \bar{y}_i)^2 \end{aligned}$$

Rearranging 10, the following set of P equations, linear in the constants, is obtained

$$\sum_{h=1}^P a_{hq} k_h = g_q \quad (11)$$

where

$$\begin{aligned} a_{hq} &= \frac{\sum_{i=1}^M \sum_{j=1}^N \frac{\partial \hat{y}_{ij}}{\partial k_h} \frac{\partial \hat{y}_{ij}}{\partial k_q}}{Q_i} \\ g_q &= \frac{\sum_{i=1}^M \sum_{j=1}^N y_{ij} (\partial \hat{y}_{ij} / \partial k_q)}{Q_i} \end{aligned}$$

with the free index q taking values from 1 to P . The solution of this set of P equations for the constants yields those constants which maximize the sum of the squared correlation coefficients. This computation was conveniently carried out on a Control Data Corporation 1604 Computer for several models.

KINETIC MODELS

One interesting feature of the data obtained was the remarkable variation in the reaction velocity with changes in the initial concentration of reaction mixture. No reasonable kinetic model which would take this phenomenal

variation into account (containing only the concentrations of the three determined components) was evident. The data could be successfully handled, however, if each initial reaction mixture could be treated as an independent case and represented by a kinetic model which involved only the concentrations of $(C_2H_5)_2SO_4$, H_2SO_4 , and $C_2H_5SO_4H$. Thus, if there was some property of the system which greatly affected the rate and yet was only a function of the initial concentration (and remained constant during any given reaction), then a kinetic model could be established which would give sets of rate constants, although they would have to be in the end expressed in terms of the initial concentration. There was some justification for this type of approach. Hellin and Jungers (9) reported that data for Reaction 3 could be correlated by the model

$$u = \frac{d(C_{C_2H_5SO_4H})}{dt} = -k_{F_3}(C_{C_2H_5SO_4H})^2(C_{H^+}) + k_{R_3}(C_{(C_2H_5)_2SO_4})(C_{H_2SO_4})(C_{H^+}) \quad (12)$$

where C_{H^+} was proportional to the initial acid concentration. Although their work was for reactions with higher initial acid concentrations than those used in this study, it was felt that a similar model might be applicable. Accordingly, a number of kinetic models were tested; four simple ones are shown in Table I.

Table II shows the results of the data analysis for each of the four models. Model A clearly gives the best data representation. Although for some reaction mixtures a moderately good fit is given by one of the other models, the results are poor for other starting reaction mixtures. The reason for this is evident in light of the high correlation for Model A. Model C is simply the right side of Model A divided by $C_{(C_2H_5)_2SO_4}$. Reaction mixtures 4a and 4b had high initial DES concentrations; hence the DES concentration varied only a small amount throughout the reaction and the effect was to divide the presumably correct Model A by a relatively constant number. The fit was worse however, as the initial DES concentration became smaller and a larger per cent conversion of DES occurred as the reaction proceeded. An exactly analogous argument explains the rather high correlation of mixtures 1a and 1b by Model C, since this model was Model A divided by $C_{H_2SO_4}$, a quantity which was relatively constant for these mixtures. Lower initial acid concentrations resulted in considerably lower sums of the squared correlation coefficients. Because of the

high variation in $C_{C_2H_5SO_4H}$ for each mixture, Model B gave a poor correlation for each initial concentration.

Tests were also made of the consistency of the rate constants in Model A throughout any given run. It was possible to set up, for each observation time, linear equations in the two unknowns, k_{F_3} and k_{R_3} . Several different pairs of these linear equations were solved for k_{F_3} and k_{R_3} , and thus several values for k_{F_3} and k_{R_3} were determined. These values compared favorably with k_{F_3} and k_{R_3} from the procedure which maximized the sum of the correlation coefficients.

Thus it was found that the data were very well represented by Model A, where k_{F_3} and k_{R_3} were functions of the initial acid concentration. Figure 2 compares these kinetic constants with those of Hellin and Jungers (9). Although none of their data was taken at 30° C., there is good agreement among the data as seen by interpolating between their data at 22.9° C. and 34° C.

MECHANISM

There is evidence (1, 5, 9) that the actual reaction mechanism for Reaction 3 is that of the formation of a carbonium ion and its reaction with bisulfate or ethyl sulfate ions. The following equations give, without attempting complex stereochemical representations of the reactions, several of the reactions that may be involved.

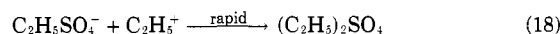
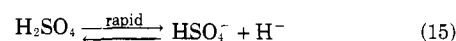
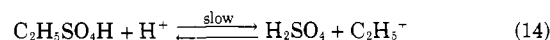
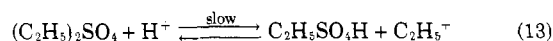


Table I. Four Kinetic Models for Reaction 3

Model A	
$\frac{d(C_{C_2H_5SO_4H})}{dt}$	$= -2 \frac{d(C_{(C_2H_5)_2SO_4})}{dt} = -2 \frac{d(C_{H_2SO_4})}{dt}$
	$= -k_{F_3}(C_{C_2H_5SO_4H})^2 + k_{R_3}(C_{(C_2H_5)_2SO_4})(C_{H_2SO_4})$
Model B	
$\frac{d(C_{C_2H_5SO_4H})}{dt}$	$= -k_{F_3}(C_{C_2H_5SO_4H}) + k_{R_3} \frac{(C_{(C_2H_5)_2SO_4})(C_{H_2SO_4})}{(C_{C_2H_5SO_4H})}$
Model C	
$\frac{d(C_{C_2H_5SO_4H})}{dt}$	$= -k_{F_3} \frac{(C_{C_2H_5SO_4H})^2}{(C_{(C_2H_5)_2SO_4})} + k_{R_3}(C_{H_2SO_4})$
Model D	
$\frac{d(C_{C_2H_5SO_4H})}{dt}$	$= -k_{F_3} \frac{(C_{C_2H_5SO_4H})^2}{(C_{H_2SO_4})} + k_{R_3}(C_{(C_2H_5)_2SO_4})$

Table II. Squared Correlation Coefficients for the Kinetic Models

Mole % H_2SO_4	Reaction Mixtures			
	1a and 1b 71	2a and 2b 46	3a and 3b 50	4a and 4b 33
	Model A			
$(C_2H_5)_2SO_4$	0.9758	0.9711	0.9833	0.9361
H_2SO_4	0.9826	0.9543	0.9781	0.9677
$C_2H_5SO_4H$	0.9797	0.9700	0.9818	0.9651
Sum	2.9381	2.9014	2.9432	2.8689
	Model B			
$(C_2H_5)_2SO_4$	0.8869	0.2588	0.3691	-2.0899
H_2SO_4	0.8555	0.3720	0.3786	-2.3663
$C_2H_5SO_4H$	0.8754	0.2932	0.3746	-2.3040
Sum	2.6178	0.9240	1.1223	-6.7602
	Model C			
$(C_2H_5)_2SO_4$	0.8193	0.8942	0.9181	0.8819
H_2SO_4	0.8372	0.8521	0.9084	0.9281
$C_2H_5SO_4H$	0.8267	0.8792	0.9139	0.9199
Sum	2.4832	2.6255	2.7404	2.7299
	Model D			
$(C_2H_5)_2SO_4$	0.9522	0.9157	0.9216	0.7875
H_2SO_4	0.9638	0.8773	0.9121	0.8524
$C_2H_5SO_4H$	0.9577	0.9022	0.9176	0.8356
Sum	2.8737	2.7952	2.7513	2.4755

Reactions 13 and 14 have been indicated as slow, rate controlling reactions in which the proton concentration of solution is of primary importance. It is postulated for mixtures initially rich in DES that the proton concentration

is radically decreased over that for mixtures with high initial acid concentration. This hypothesis seems reasonable, since the acidic nature of the $C_2H_5SO_4H$ formed from H_2SO_4 during Reaction 3 would tend to keep the proton concentration constant throughout Reaction 3. This constant proton concentration throughout the reaction coupled with a very great decrease in proton concentration with increase in DES concentration can explain the constancy of k_{F_3} and k_{R_3} for each individual reaction and yet their large variation with initial H_2SO_4 concentration

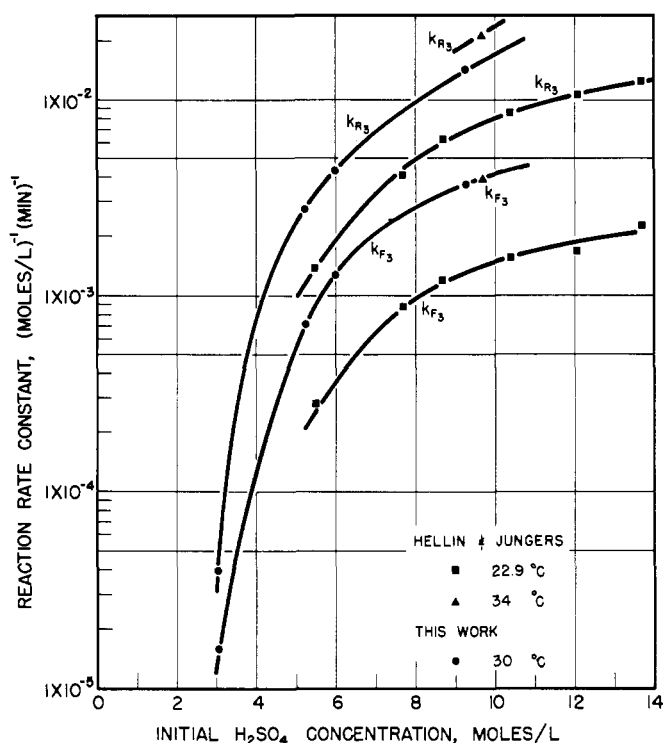


Figure 2. Rate constants for the $C_2H_5SO_4H - (C_2H_5)_2SO_4 - H_2SO_4$ reaction as functions of initial H_2SO_4 concentration

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Thermodynamic Properties of Solid Monoxides, Monosulfides, Monoselenides, and Monotellurides of Ge, Sn, and Pb

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The thermodynamic properties of the oxides, sulfides, selenides, and tellurides of Ge, Sn, and Pb are systematically compiled. A number of these values are computed from the most recent published data.

A NUMBER of binary compounds formed between elements of Groups IVA (Ge, Sn, Pb) and VIA (S, Se, Te) of the periodic table are known to be useful semiconducting and photoconducting materials. Recent measurements on the volatility characteristics of sulfides, selenides, and tellurides of this group of compounds make it possible to compute all of the thermodynamic properties of these binary solids with some degree of accuracy. Because of their high dissociation energies these compounds exist in the vapor phase predominantly as the molecular species.

The new reliable data concerning vapor pressures and dissociation energies allow the systematic compilation of thermodynamic data for the IVA-VIA binary compounds. A number of values, such as the heat of formation of SnSe and GeS are reported here for the first time. The

thermodynamic properties of these compounds are of interest to solid state physicists as well as to chemists.

RESULTS

The standard heat of formation and entropies of most of the compounds have been tabulated (15, 18, 27). Although the vapor pressures of all of the compounds have been reported, the heats of sublimation at 298° K. have not been reported in many cases. Since the high temperature heat capacities of most of these compounds are not available, we have made reasonable estimates in computing the heat of sublimation at 298° K. by the third law method. The high temperature entropy and enthalpy functions of Kelley (14) were used.