

High Temp.

HETEROLYTIC DISSOCIATION OF POTASSIUM SULFATE IN THE GASEOUS PHASE  
AND ENTHALPY OF FORMATION OF  $\text{SO}_3^-$ ,  $\text{SO}_4^-$ , AND  $\text{KSO}_4^-$

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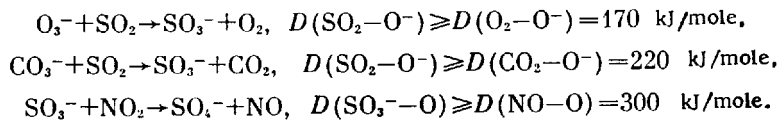
UDC 541.51

The equilibrium constants of gaseous ion-molecular reactions in saturated potassium sulfate vapor, involving  $\text{SO}_2^-$ ,  $\text{SO}_3^-$ ,  $\text{SO}_4^-$ ,  $\text{KSO}_4^-$ , and  $\text{K}_3\text{S}_2\text{O}_8^-$  ions, were measured. The enthalpies of formation of the ions were determined to be  $-601.1 \pm 7.4$  kJ/mole for  $\text{SO}_3^-$ ,  $-744.1 \pm 9.8$  kJ/mole for  $\text{SO}_4^-$ , and  $-992.3 \pm 11.0$  kJ/mole for  $\text{KSO}_4^-$ . The possible errors in the values obtained are analyzed.

Recently, the enthalpies of formation have been determined for a number of fluoride [1] and oxide [2] negative ions in the gaseous phase, making it possible to calculate an important characteristic — the energy of dissociation into positive and negative ions — for a number of compounds. This quantity is of great interest since it makes it possible to investigate the potential of the ionic model for predicting the properties of salts of alkali metals.

Experimental results have been obtained only for monobasic salts, so the present investigation of negative ions in the saturated vapor of the dibasic salt  $\text{K}_2\text{SO}_4$  was undertaken.  $\text{SO}_2^-$ ,  $\text{SO}_3^-$ ,  $\text{SO}_4^-$ ,  $\text{KSO}_4^-$ , and  $\text{K}_3\text{S}_2\text{O}_8^-$  ions were recorded, no doubly charged ions being observed in the gaseous phase. As one would expect, dibasic salts in the gaseous phase dissociate only to the first stage. The presence of singly charged ions of sulfur oxides increased the authors' interest in the investigation since these ions play a large role in the chemistry of the ionosphere. It is believed that  $\text{SO}_4^-$  ions, together with  $\text{NO}_3^-$  and  $\text{CO}_3^-$ , will complete the chain of ion-molecular conversion in the presence of sulfur impurities [3].

We briefly review existing data in the literature on negative ions of sulfur oxides. The enthalpy of formation of  $\text{SO}_2^-$  was reliably determined by photoelectron spectroscopy of the negative ions and the value obtained has been confirmed in a number of other investigations (see [4] for more details).  $\text{SO}_3^-$  and  $\text{SO}_4^-$  have been much less studied. In [5] the threshold of the reaction  $\text{SO}_3 + \text{Cs} = \text{SO}_3^- + \text{Cs}^+$  was determined, whence the lower limit of the electron affinity of  $\text{SO}_3$  was determined:  $\text{EA} \geq 164$  kJ/mole. The enthalpy of formation of  $\text{SO}_4^-$  is unknown. In [3] the rate constants of some ion-molecular reactions involving  $\text{SO}_3^-$  and  $\text{SO}_4^-$  were measured. If one considers the occurrence of a reaction as an indication that the enthalpy of the reaction is negative,  $\Delta H_0^\circ < 0$ , then a number of inequalities can be obtained and described in terms of bond-breaking energies:



We observe that in [6, 7] ion-molecular equilibria in saturated  $\text{K}_2\text{SO}_4$  involving positive ions were studied.  $\text{K}^+$  and  $\text{K}_3\text{SO}_4^+$  ions were observed, and the energy of removing a potassium ion  $D(\text{K}^+ - \text{K}_2\text{SO}_4)$  was measured to be 205 kJ/mole.

Experiment. An MKh-1303 mass spectrometer was used for the investigations, adapted for studying ion-molecular equilibria [8]. Chemically pure grade potassium sulfate was evaporated from a platinum crucible of dimensions  $12 \times 12$  mm with a ratio of evaporating area to effusion aperture area in the range from 900 to 16. The temperature of the crucible was measured with a welded platinum-platinum/rhodium (10% Rh) thermocouple. The accuracy of the temperature measurement was estimated as  $\pm 3^\circ\text{K}$ . The temperature was maintained constant to within  $\pm 1^\circ\text{K}$  by means of a VRT-3 automatic controller.

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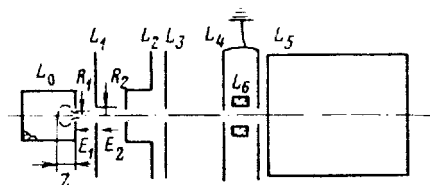


Fig. 1. Arrangement of the ion source:  $L_0$ ) crucible, potential  $U_0 = -2$  kV;  $L_2, L_3$ ) focusing electrodes,  $U_2 = -1.8-1.0$  kV,  $U_3 = -1.4-0.9$  kV;  $L_1$ ) attractive electrode,  $U_1 = -2-1.3$  kV;  $L_4$ ) exit slit,  $U_4 = 0$ ;  $L_5, L_6$ ) deflecting condenser plates,  $U_5 = -40-40$  V,  $U_6 = -150-150$  V.

TABLE 1. Operating Parameters of the Ion Source (see Fig. 1 for notation) and Negative-Ion Mass Spectra

Regime	†	‡	‡	‡
$R_1, \text{ mm}$	0.2	0.2	0.2	1.5
$R_2, \text{ mm}$	1.5	1.5	1.5	1.5
$E_1, \text{ V/mm}$	0	14	260	44
$E_2, \text{ V/mm}$	17	47	73	87
$z, \text{ mm}$	0	0.8	3.3	12
$I(^{32}\text{SO}_2^-)$ •	65	130	62	210
$I(^{32}\text{SO}_3^-)$ •	130	300	130	520
$I(^{32}\text{SO}_4^-)$ •	3	7	3	11
$I(^{39}\text{K}^{32}\text{SO}_4^-)$ •	100	230	95	310
$I(^{39}\text{K}_3^{32}\text{S}_2\text{O}_8^-)$ •	3	6	3	4

\*Ion currents ( $\times 10^{11}$  A), measured with the amplifier;  $v(\text{SO}_3^-) = I_m/I_e \approx 2.5 \cdot 10^4$ .

†Ion currents at  $T = 1326.1^\circ\text{K}$ .

‡Ion currents at  $T = 1281.8^\circ\text{K}$ .

The arrangement of the ion source is shown in Fig. 1. Concentric apertures were made in the crucible and in the attractive electrode, and 1.5-mm-wide slits were made in the electrodes  $L_2-L_4$ . The electric field penetrated into the crucible [9], i.e., the equipotential  $U > U_0$  takes a form similar to the dashed line in Fig. 1. The space inside the crucible is, as it were, divided into two zones with different electric fields. We determined the low and high fields. As a measure of the field one can take the thermal energy of the moving ion, being  $\approx kT$ . Then the energy acquired by an ion in the low field  $e(U - U_0) = e\Delta U < kT$ . For quantitative calculations we take  $e\Delta U = 0.2$  kT. Then at  $T = 1200^\circ\text{K}$  we obtain the limit of the low field  $\Delta U = 0.02$  V.

As a qualitative measure of the penetration of the field into the chamber, one can take the distance  $z$  (see Fig. 1) along the axis of the crucible where the equipotential  $U$  passes, with  $U - U_0 = 0.02$  V. To calculate this quantity, we use the formula for the distribution of the potential on the axis of a diaphragm [10]

$$\Delta U = -\frac{E_1 z}{2} + \frac{R_1 E_1}{\pi} \left( \frac{z}{R_1} \arctg \frac{z}{R_1} + 1 \right) = 0.02.$$

With this kind of source, many measurements of ion-molecular equilibria involving both positive (see the compilation [11]) and negative (see the compilation [1]) ions have been carried out. In the study of the NaF-AlF<sub>3</sub> system [8], an equilibrium was found between the neutral and negatively charged components of the saturated vapor. However, in the various works there is a disagreement over the choice of conditions for carrying out the measurements (see discussion in [12]). We therefore made a methodological investigation in order to study the possible changes in the ratios of the ion currents of the negative ions under different conditions of operation of the ion source. Four regimes of operation were chosen, whose parameters are given in Table 1. It can be seen that penetration into the chamber was gradually increased. In the fourth regime the equipotential  $U = 1999.95$  V passed at a distance  $z = 12$  mm (boundary of the crucible), i.e.,  $\Delta U = 0.05$  V = 0.5 kT. This indicates that the space of the crucible with the low field has practically disappeared.

Negative ions  $\text{SO}_2^-$ ,  $\text{SO}_3^-$ ,  $\text{SO}_4^-$ ,  $\text{KSO}_4^-$ , and  $\text{K}_3\text{S}_2\text{O}_8^-$  were recorded. The ion currents were measured with a VEU-6 amplifier. The ratios of the "true" ion currents can be obtained in the following form:

$$I_e(A^-)/I_e(B^-) = [I_m(A^-)/I_m(B^-)] [\gamma(B^-)/\gamma(A^-)],$$

where  $I_m$  is the current measured with the amplifier,  $I_e$  with the electrometer, and  $\gamma(B^-)/\gamma(A^-) = [M(A)/M(B)]^{1/2}$ . To verify the last equation, the ion currents were measured with an electrometer:

$$\ln [\gamma(\text{KSO}_3^-)/\gamma(\text{SO}_3^-)] = -0.36; \quad s=0.15; \quad n=2;$$

$$1/2 \ln [M(\text{SO}_3^-)/M(\text{KSO}_3^-)] = -0.37;$$

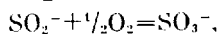
$$\ln [\gamma(\text{SO}_3^-)/\gamma(\text{SO}_2^-)] = -0.11; \quad s=0.10; \quad n=2;$$

$$1/2 \ln [M(\text{SO}_2^-)/M(\text{SO}_3^-)] = -0.11;$$

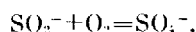
where  $s$  is the standard deviation for one measurement and  $n$  is the number of measurements. It can be seen that the results are consistent with the ratio taken for the amplifier coefficients.

In each operating regime the ion currents were recorded for several temperatures. The temperature was changed in steps of 50-100°K.

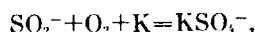
Initial Treatment of Experimental Data. From the measured values of the ion currents, the equilibrium constants of the following reactions were calculated:



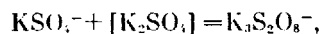
$$\ln K_p(1) = \ln [I(^{32}\text{SO}_3^-)/I(^{32}\text{SO}_2^-)] - 1/2 \ln p(\text{O}_2) + \ln 1.25; \quad (1)$$



$$\ln K_p(2) = \ln [I(^{32}\text{SO}_4^-)/I(^{32}\text{SO}_2^-)] - \ln p(\text{O}_2) + \ln 1.5; \quad (2)$$



$$\ln K_p(3) = \ln [I(^{39}\text{K}^{32}\text{SO}_4^-)/I(^{32}\text{SO}_2^-)] - \ln p(\text{O}_2) - \ln p(\text{K}) + \ln 2.266; \quad (3)$$



$$\ln K_p(4) = \ln [I(^{39}\text{K}_3^{32}\text{S}_2\text{O}_8^-)/I(^{39}\text{K}^{32}\text{SO}_4^-)] - \ln 0.36. \quad (4)$$

The conversion from ratios of ion currents to ratios of pressures was made using the formula [9]

$$p(A^-)/p(B^-) = [I_m(A^-)/I_m(B^-)] [M(A)/M(B)]^{1/2} [\gamma(B^-)/\gamma(A^-)] [i(B^-)/i(A^-)],$$

where  $i$  is the content of the measured isotope. Hence the numerical constants appearing in Eqs. (1)-(4) were obtained.

At each temperature the mass spectrum was recorded several times. The logarithms of the ratios of ion currents were averaged and the standard deviation of the logarithm of the ratio was calculated for one measurement. Then the constants were calculated according to Eqs. (1)-(4). (The calculation of the pressures of K and O<sub>2</sub> is given in Appendix 2.)

The data obtained in this way are combined in Table 2, where, instead of the dimensionless logarithms of the constants, the quantities  $Y = R \ln K$  are shown, having the dimensions of J/mole·°K ( $R = 8.31441$  J/mole·°K [4]):

$$Y = R \ln K, \quad \bar{Y}_i = \sum_j Y_{ij}/n_i, \quad s_i = \left[ \sum_j (Y_{ij} - \bar{Y}_i)^2 / \nu_i \right]^{1/2}, \quad \nu_i = n_i - 1.$$

Here  $j = 1, \dots, n_i$  is the number of measurements at a given temperature,  $s_i$  is the standard deviation for one measurement, and  $\nu_i$  is the number of degrees of freedom. The standard deviations have dimensions of J/mole·°K. An error in  $Y = R \ln K$  at magnitude 1 J/mole·°K assumes an error in the constant of 13%, at 2 J/mole·°K of 24%, and at 0.5 J/mole·°K of 6%.

Analysis of Results. It was assumed that all the measured logarithms of the equilibrium constants have identical limiting standard deviations  $\sigma_i$  for one measurement, independent of temperature, regime, and reaction. The magnitude of  $\sigma_i$  expresses the random scatter in the constant arising from instabilities in the mass spectrometer, i.e.,  $\sigma_i$  does not change for a given apparatus. As a qualitative estimate of it, the combined standard deviation

TABLE 2. Results of Initial Treatment of Experimental Data\*

T, K	Reaction											
	(1)			(2)			(3)			(4)		
	$R \ln K_i$	$s_i$	$n_i$	$R \ln K_i$	$s_i$	$n_i$	$R \ln K_i$	$s_i$	$n_i$	$R \ln K_i$	$s_i$	$n_i$
	J/mole · K			J/mole · K			J/mole · K			J/mole · K		
Regime 1												
1218.8	76.06	0.50	3	88.40	0.46	4	271.58	0.35	3	-20.30	0.59	4
1326.1	63.58	0.12	4				227.91	0.29	4			
Regime 2												
1163.9	81.39	-	1	-	-	-	298.96	-	1	-	-	-
1194.4	81.60	0.76	2	-	-	-	286.07	0.80	2	-	-	-
1236.9	74.76	-	1	108.13	-	1	267.75	-	1	-24.17	-	1
1326.1	65.24	0.62	3	91.15	0.90	3	229.24	0.17	3	-22.58	0.27	3
Regime 3												
1191.4	80.96	1.22	2	-	-	-	286.56	0.53	2	-	-	-
1236.9	75.01	0.09	2	108.35	0.06	2	265.61	1.35	2	-21.68	0.96	2
1281.8	69.29	0.02	2	98.13	1.79	2	246.70	1.25	2	-20.74	0.03	2
1326.1	64.20	0.43	2	89.62	0.67	2	227.62	0.41	2	-20.51	0.27	2
Regime 4												
1089.3	95.72	0.60	2	-	-	-	335.61	0.91	2	-	-	-
1145.4	88.24	-	1	128.75	-	1	306.91	-	1	-30.37	-	1
1163.9	84.40	0.37	2	122.08	0.89	2	295.58	0.16	2	-32.69	1	2
1236.9	75.41	0.72	4	108.81	1.93	4	263.67	0.60	4	-28.49	1	3
1281.8	68.94	-	1	98.47	-	1	243.54	-	1	-28.05	-	1

\* $s_i$  is the standard deviation,  $n_i$  is the number of measurements.

TABLE 3. Standard Deviations of Regression (in J/mole · °K)\*

Regime	Reaction							
	(1)		(2)		(3)		(4)	
	$s_r^{II}$	$s_r^{III}$	$s_r^{I}$	$s_r^{II}$	$s_r^{I}$	$s_r^{III}$	$s_r^{II}$	$s_r^{I}$
1	-	1.14 (1)	-	-	-	1.90 (1)	-	-
2	0.71 (2)	1.19 (3)	-	1.53 (1)	0.47 (2)	1.15 (3)	-	-
3	0.11 (2)	0.27 (3)	0.54 (1)	0.40 (2)	0.85 (2)	0.79 (3)	0.58 (1)	-
4	0.82 (3)	1.12 (4)	1.98 (2)	2.79 (3)	1.34 (3)	1.71 (4)	1.89 (2)	-

\*The number of degrees of freedom is given in parentheses.

$$s_p = \left( \sum_i s_i^2 v_i / \sum_i v_i \right)^{1/2} = 0.93 \text{ J/mole} \cdot \text{K}, \quad v_p = \sum_i v_i = 58$$

was used. The sum was carried out over all reactions, temperatures, and regimes. The magnitude obtained corresponds to the error in the equilibrium constant for one measurement (13%). Unfortunately, in work with high-temperature mass spectrometers such quantities are not, as a rule, calculated and so there is no possibility of comparing with data in the literature.

To describe the measured equilibrium constants, two models were used. The first is an analysis of the equilibrium constants using the second law of thermodynamics:

$$Y^{II} = R \ln K = -\Delta H_T^\circ(\text{II})/T + \Delta S_T^\circ(\text{II}). \quad (5)$$

Here the parameters  $\Delta H_T^\circ(\text{II})$  and  $\Delta S_T^\circ(\text{II})$  are to be determined. To determine them, the residual sum of squares  $\sum_i (Y_i^{II} - \bar{Y}_i)^2 n_i$  is minimized [13], leading to the standard solution.

The second model is an analysis of the equilibrium constants using the third law of thermodynamics:

$$Y^{III} = R \ln K = -\Delta H_0^\circ(\text{III})/T + \Delta \Phi_T^\circ(\text{III}), \quad (6)$$

TABLE 4. Enthalpies of the Reactions (1)-(4) (in kJ/mole)\*

Reaction	Reaction						
	(1)		(2)		(3)		(4)
	$-\Delta H_T^\circ(\text{II})$	$-\Delta H_0^\circ(\text{III})$	$-\Delta H_T^\circ(\text{II})$	$-\Delta H_0^\circ(\text{III})$	$-\Delta H_T^\circ(\text{II})$	$-\Delta H_0^\circ(\text{III})$	$-\Delta H_T^\circ(\text{II})$
1	188.0 (10.7)	199.9	-	372.5	657.8 (10.7)	680.6	-
2	186.9 (8.1)	201.5	312.1 (19.7)	375.6	664.7 (8.1)	682.1	-29.3 (19.7)
3	197.1 (10.7)	201.0	344.6 (17.2)	374.0	688.5 (10.3)	682.1	-21.6 (17.2)
4	189.7 (6.3)	200.6	297.5 (10.5)	373.0	660.4 (6.3)	678.5	-49.5 (10.8)

\*The standard deviation is given in parentheses.

TABLE 5. Subsidiary Thermodynamic Information [4]

Compound	$\Delta_f H_0^\circ$	$\Delta(\Delta_f H_0^\circ)$	$\Phi_{1300}^0$	$\Delta\Phi_{1300}^0$
	kJ/mole		J/mole · K	
[K <sub>2</sub> SO <sub>4</sub> ]	-1427.183	0.5	274.152	1.6
SO <sub>2</sub>	-294.264	0.2	272.740	0.2
O <sub>2</sub>	0	0	167.526	0.02
K	89.891	0.5	170.052	0.02
SO <sub>2</sub> <sup>-</sup>	-400.064	3.5	281.800	2.0

where one parameter  $\Delta\Phi_T^\circ$  (III) is given a priori and  $\Delta H_0^\circ$  is to be determined. For this it is necessary to minimize, as in the first case, the residual sum of squares  $\sum_i (Y_i^{\text{III}} - \bar{Y}_i)^2 n_i$ , giving

$$\Delta H_0^\circ(\text{III}) = - \left[ \sum_i (\bar{Y}_i - \Delta\Phi_T^\circ) n_i T_i^{-1} \right] / \sum_i n_i T_i^{-2} \quad (7)$$

The last formula is rather different from the one conventionally used in high-temperature mass-spectrometer investigations:

$$\Delta H_0^\circ(\text{III}) = - \left[ \sum_i (\bar{Y}_i - \Delta\Phi_T^\circ) n_i T_i \right] / \sum_i n_i \quad (8)$$

The conventional formula is obtained by minimizing the residual sum of squares of the form  $\sum_i (Y_i^{\text{III}} - \bar{Y}_i)^2 n_i T_i$ , in which the constants enter with the temperatures as weights. Thus, Eq. (8) assumes nonequivalence in the constants. The equilibrium constants measured at high temperatures give a large contribution to the result, whereas Eq. (7), used in this work, is free of this defect.

For both models the standard deviations of regression

$$s_{r^{\text{II}}} = \left[ \sum_i (Y_i^{\text{II}} - \bar{Y}_i)^2 n_i / (N-2) \right]^{1/2}, \quad s_{r^{\text{III}}} = \left[ \sum_i (Y_i^{\text{III}} - \bar{Y}_i)^2 n_i / (N-1) \right]^{1/2}$$

were calculated. These quantities indicate the mean deviation of the measured equilibrium constants from Eqs. (5) and (6), respectively, and also serve as estimates of the limiting standard deviation  $\sigma_1$  of one measurement [13]. This makes it possible to use the ratios  $s_{r^{\text{II}}}/s_p$ ,  $s_{r^{\text{III}}}/s_p$ , and  $s_{r^{\text{III}}}/s_{r^{\text{II}}}$  to verify the models and compare them with one another.

The quantities  $s_{r^{\text{II}}}$  and  $s_{r^{\text{III}}}$  are given in Table 3,  $\Delta H_T^\circ$  (II) and  $\Delta H_0^\circ$  (III) in Table 4. The enthalpies of reaction obtained from the IInd and IIIrd laws can be directly compared, since for the reactions (1)-(3) the change in enthalpy  $\Delta H_T^\circ - \Delta H_0^\circ$  is  $\approx 1$  kJ/mole.

We observe that the third law gives better agreement in the reactions (1)-(3) for all regimes. This corresponds to the fact that the maximum difference in the constants of these reactions in the different regimes reaches 40%. This is larger than the statistical scatter - 13% ( $s_p = 0.93 \text{ J/mole}\cdot^\circ\text{K}$ ). There is a systematic error in the equilibrium constants related to the operation of the mass spectrometer, and the quantity 40% characterizes this systematic error. Hence it follows that the systematic error in the equilibrium constants of reactions (1)-(3) related to the operation of the ion source does not exceed 40% or  $3 \text{ J/mole}\cdot^\circ\text{K}$  in the quantity  $R \ln K$ .

We compare the regimes with one another. From the ratio  $s_r^{II}/s_p$  it is evident that a straight line adequately describes the experimental constants in all regimes. However, the slopes of these lines [ $\Delta H_T^\circ(II)$ ] are different, but the trend of the slope is the same in all four reactions. Hence, it follows that in some regimes there is a systematic error in the change of the constants with temperature. As an evaluation of the regime, we take the agreement between the second and third laws. As can be seen (Tables 3 and 4), the best agreement in reactions (1)-(3) is attained in regime 3. Hence, the ratios of the ion currents measured in regime 3 are closest to the equilibrium ratios of the ion pressures. At present it is not entirely clear which feature of regime 3 led to this result. Therefore, we restrict ourselves to establishing the facts without a detailed examination of this question.

Discussion of Results. Table 5 shows subsidiary thermodynamic information used in this work. As recommended values of the enthalpies of reactions (1)-(3) the values obtained in the third regime using the third law were chosen.

The error in these quantities is comprised of the following factors: the random error, the systematic errors in the constants related to the ion source  $\Delta Y_s$ , to the amplifier  $\Delta Y_m$ , and to the calculation of the pressure  $\Delta Y_p$ , and the errors in the thermodynamic functions  $\Delta(\Delta\Phi)$ . Since the random errors in this case are small, they can be neglected; then, assuming the errors listed to be independent, we can write

$$\Delta(\Delta H) = T(\Delta(\Delta\Phi)^2 + \Delta Y_s^2 + \Delta Y_m^2 + \Delta Y_p^2)^{1/2},$$

where  $\Delta(\Delta\Phi)$  was calculated on the basis of Table 5 and Appendix 1;  $\Delta Y_s$  on the basis of the previous section was estimated as  $3 \text{ J/mole}\cdot^\circ\text{K}$ ;  $\Delta Y_m$  was estimated to be  $1.6 \text{ J/mole}\cdot^\circ\text{K}$  for reactions (1) and (3) and  $3 \text{ J/mole}\cdot^\circ\text{K}$  for reaction (2).  $\Delta Y_p$  is calculated in Appendix 2. Thus, the following quantities were obtained:

$$\Delta_r H_0^\circ(1) = -201.0 \pm 6.5, \quad \Delta_r H_0^\circ(2) = -344.0 \pm 9.2, \quad \Delta_r H_0^\circ(3) = -682.1 \pm 10.5.$$

For the  $\text{K}_2\text{S}_2\text{O}_8^-$  ion the thermodynamic functions were not calculated. Therefore, for reaction (4) we introduce an equation describing the equilibrium constants in regime 3 (in  $\text{J/mole}\cdot^\circ\text{K}$ ):

$$Y(4) = R \ln K_p(4) = -21600/T - 4.1.$$

The standard deviation of regression for this equation can be calculated as a function of temperature with the following formula:

$$s[Y(4)] = 0.93 \left[ \frac{1}{n} + \frac{(T^{-1} - 1281^{-1})^2}{5.44 \cdot 10^{-5}} \right]^{1/2} \text{ J/mole}\cdot^\circ\text{K}.$$

From the values given above for the enthalpies of reactions (1)-(3) and the data of Table 5, one can calculate the enthalpies of formation of the negative ions:

$$\Delta_r H_0^\circ(\text{SO}_3^-) = -601.1 \pm 7.4, \quad \Delta_r H_0^\circ(\text{SO}_4^-) = -744.1 \pm 9.8, \\ \Delta_r H_0^\circ(\text{KSO}_4^-) = -992.3 \pm 11.0.$$

We observe that the enthalpies of formation of  $\text{K}$ ,  $\text{O}_2$ ,  $\text{SO}_2$ , and  $[\text{K}_2\text{SO}_4]$ , given in the handbook [14], coincide with those used in the present work [4] to within  $0.1 \text{ kJ/mole}$ .

Using the enthalpies of formation of  $\text{O}$ ,  $\text{S}$ ,  $\text{SO}$ ,  $\text{SO}_2$ ,  $\text{S}^-$ ,  $\text{O}^-$ , and  $\text{SO}^-$  ( $246.8$ ,  $274.8$ ,  $4.6$ ,  $-390.1$ ,  $74.4$ ,  $105.6$ , and  $-100.6 \text{ kJ/mole}$  at  $0^\circ\text{K}$  [4]) and the ionic enthalpies obtained in this work, one can calculate the energies of successive bond breaking (in  $\text{kJ/mole}$ ):

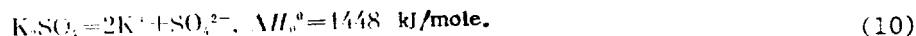
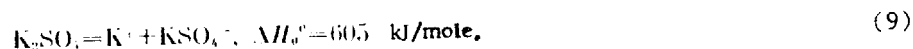
$$D(\text{S}-\text{O}) = 517, \quad D(\text{S}-\text{O}^-) = 481, \quad D(\text{S}^--\text{O}) = 422, \\ \text{EA}(\text{SO}) = 105, \quad D(\text{SO}-\text{O}) = 546, \quad D(\text{SO}-\text{O}^-) = 510.$$

$$D(\text{SO}_3^- - \text{O}) = 546, \text{EA}(\text{SO}_3) = 105, D(\text{SO}_2^- - \text{O}) = 343,$$

$$D(\text{SO}_2^- - \text{O}^-) = 412, D(\text{SO}_2^- - \text{O}) = 448, \text{EA}(\text{SO}_2) = 211,$$

$$D(\text{SO}_3^- - \text{O}^-) = 459, D(\text{SO}_3^- - \text{O}) = 390.$$

In [15] an ionic model was used to examine the equilibrium geometry of potassium sulfate. From the potential energy function proposed in [15] and the equilibrium geometry of  $\text{K}_2\text{SO}_4$  [4], the enthalpies of reactions (9) and (10) were calculated:



The experimental value  $\Delta H_f^\circ$  for reaction (9) is equal to 599 kJ/mole. (The enthalpies of formation of  $\text{K}_2\text{SO}_4$  and  $\text{K}^+$  at 0°K are -1082.2 and 508.7 kJ/mole [4].) The agreement obtained confirms the validity of regarding potassium sulfate as an ionic molecule. Now one can use the enthalpy of reaction (10), calculated from the ionic model, and estimate the enthalpy of formation of  $\text{SO}_4^{2-}$  to be  $\Delta_f H_f^\circ = -652$  kJ/mole. The coincidence of the theoretical and experimental values of the enthalpy  $\Delta H_f^\circ$  of reaction (9) indicates that this estimate is reliable.

The value obtained for the second electron affinity of  $\text{SO}_4$ , -92 kJ/mole, is rather large. The corresponding value for O of -800 kJ/mole [16] is significantly lower.

#### APPENDIX 1

Calculation of Thermodynamic Functions. Table 6 shows the chosen molecular constants for the  $\text{SO}_3^-$ ,  $\text{SO}_4^-$ , and  $\text{KSO}_4^-$  ions, and Table 7 the calculated thermodynamic functions.

For the  $\text{SO}_3^-$  ion the structure  $C_{3v}$  was chosen,  $R(\text{S}-\text{O}) = 0.142$  nm and  $\angle \text{OSO} = 110^\circ$ . This choice was based on a theoretical analysis of the structure of  $\text{XY}_3$  molecules [17] and experimental data for the  $\text{SO}_3$ ,  $\text{CCl}_3$ , and  $\text{SiCl}_3$  molecules [18]. The frequencies for the  $\text{SO}_3^-$  ion were estimated on the basis of the trends of frequencies in the  $\text{SO}_3$ ,  $\text{CF}_3$ ,  $\text{NF}_3$ , and  $\text{ClO}_3^-$  molecules [18].

In removing one electron from the  $\text{SO}_4^{2-}$  anion, i.e., on going to  $\text{SO}_4^-$ , an orbital degeneracy appears which must lead to a distortion of the tetrahedral structure. The authors

TABLE 6. Molecular Constants of  $\text{SO}_3^-$ ,  $\text{SO}_4^-$ , and  $\text{KSO}_4^-$

Ion	Quantity	$g_j$	$I_A I_B I_C$ $10^{11}$ $\text{g}^3 \cdot \text{cm}^6$	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$	$\nu_6$	$\nu_7$
$\text{SO}_3^-$	$C_{3v}$	2	1130	1000	610	1187(2)	504(2)			
$\text{SO}_4^-$	$C_{3v}$	2	3590	1056	839	534	1178(2)	604(2)	369(2)	
$\text{KSO}_4^-$	$C_{2v}$	1	48700	1099	962	609	520	230	460	1099

\*  $\nu_8 = 609$ ,  $\nu_9 = 62$ ,  $\nu_{10} = 1126$ ,  $\nu_{11} = 640$ ,  $\nu_{12} = 262$ .

TABLE 7. Calculated Thermodynamic Quantities

T, K	Ion		
	$\text{SO}_3^-$	$\text{SO}_4^-$	$\text{KSO}_4^-$
	$H_{298}^0 - H_0^0$ , kJ/mole		
	11.7	13.4	17.3
$-(G_T^0 - H_0^0) / T$ , J/mole · K			
298,15	229,0	238,9	267,5
400	241,1	253,1	285,5
600	260,0	276,2	315,2
800	275,3	295,3	339,5
1000	288,2	312,6	360,2
1200	299,4	325,8	378,1
1400	309,3	338,5	394,0

propose that the  $\text{SO}_4^-$  ion will take the  $C_{3v}$  structure (like the isoelectronic molecule  $\text{SO}_3\text{F}$ ). However, the product of the principal energy moments was calculated for a tetrahedral structure with  $R(\text{S-O}) = 0.147$  nm (as in  $\text{K}_2\text{SO}_4$ ). The normal vibrational frequencies of  $\text{SO}_4^-$  were taken equal to those of the isoelectronic molecule  $\text{SO}_3\text{F}$  [18].

For  $\text{KSO}_4^-$ , the  $C_{2v}$  structure was chosen with the assumption that the internuclear distance is the same as in potassium sulfate:  $R(\text{S-O}) = 0.147$  nm,  $R(\text{K-O}) = 0.245$  nm,  $\angle \text{OSO} = 109.47^\circ$  [4]. The frequencies of the normal modes of vibration were taken equal to those of potassium sulfate [4], except for the three low frequencies associated with vibrations of the  $\text{K}^+$  ion.

To calculate the errors in the thermodynamic functions, the error in the product of the principal energy moments was estimated (15, 25, and 30% for  $\text{SO}_3$ ,  $\text{SO}_4^-$ , and  $\text{KSO}_4^-$ ), and the errors in all the frequencies were taken as  $\Delta\nu = 100$   $\text{cm}^{-1}$ , except for  $\nu_8$  and  $\nu_{12}$  ( $\Delta\nu = 50$   $\text{cm}^{-1}$ ) and  $\nu_9$  ( $\Delta\nu = 20$   $\text{cm}^{-1}$ ) in  $\text{KSO}_4^-$ . The error in the harmonic oscillator-rigid rotator approximation was estimated the same as in [4] (5% of the vibrational component  $\Phi_T^\circ$ ). As a result, the error in determining  $\Phi_T^\circ$  at 1200°K was estimated as 3.7, 6.0, and 7.8 kJ/mole·°K for the  $\text{SO}_3^-$ ,  $\text{SO}_4^-$ , and  $\text{KSO}_4^-$  ions, respectively.

## APPENDIX 2

Calculation of the Composition of the Gaseous Phase on the Evaporation of  $\text{K}_2\text{SO}_4$ . Potassium sulfate evaporates congruently [4, 14, 19]. Under conditions of effusion, this means that the composition of the condensed phase does not change. Consequently, the composition of the beam flowing out of the effusion chamber must be equal to that of the condensed

phase. One can write  $\rho_{\text{K}}^{\text{tot}} = \rho_{\text{O}_2}^{\text{tot}} = 2\rho_{\text{S}}^{\text{tot}}$ . Here  $\rho^{\text{tot}}$  denotes the full current of the element in all its forms. The main components of the vapor are  $\text{K}_2\text{SO}_4$ ,  $\text{SO}_2$ ,  $\text{O}_2$ , and K. The content of the remaining components is several orders of magnitude lower. Then

$$\begin{aligned}\rho_{\text{K}}^{\text{tot}} &= \rho_{\text{K}} + 2\rho_{\text{K}_2\text{SO}_4}, & \rho_{\text{O}_2}^{\text{tot}} &= \rho_{\text{O}_2} + \rho_{\text{SO}_2} + 2\rho_{\text{K}_2\text{SO}_4}, \\ \rho_{\text{S}}^{\text{tot}} &= \rho_{\text{SO}_2} + \rho_{\text{K}_2\text{SO}_4},\end{aligned}$$

where  $\rho$  is the current of molecules flowing out of the effusion camera per unit time through unit area. The current  $\rho$  is related to the partial pressure by the Hertz-Knudsen equation  $\rho = p(2\pi\text{RMT})^{-1/2}$ . After transforming, we obtain

$$p(\text{O}_2)M(\text{O}_2)^{-1/2} = p(\text{SO}_2)M(\text{SO}_2)^{-1/2} = 1/2p(\text{K})M(\text{K})^{-1/2}.$$

Now we can use the equilibrium constant of reaction (11), which was calculated on the basis of data in the handbook [4]:

$$[\text{K}_2\text{SO}_4] = 2\text{K} + \text{O}_2 + \text{SO}_2. \quad K_p(11) = p(\text{K})^2 p(\text{SO}_2) p(\text{O}_2). \quad (11)$$

We introduce the partial pressures calculated at  $T = 1300^\circ\text{K}$  (in Pa):  $p(\text{K}_2\text{SO}_4) = 0.59$ ,  $p(\text{K}) = 0.18$ ,  $p(\text{O}_2) = 0.082$ , and  $p(\text{SO}_2) = 0.12$ .

We calculate the error in the determination of the pressure. The error  $\Delta[\Delta H_0^\circ(11)] = 0.73$  kJ/mole and  $\Delta[\Delta\Phi_T^\circ(11)] = 1.6$  J/mole·°K (see Table 5). This leads to the magnitude of the error in the pressure of oxygen of 10%, or to the error in the quantity  $\Delta[\text{R} \ln p(\text{O}_2)]$  of 0.6 J/mole·°K.

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#### CALCULATION OF THE STRUCTURE AND THERMODYNAMIC PROPERTIES OF LIQUID RARE-EARTH METALS

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The Mansouri-Canfield variational method and the pseudopotential method (Ashcroft model pseudopotential) were used to calculate the structure and thermodynamic properties of La, Ce, Pr, Nd, and Sm. Structural parameters near the melting point and the Ashcroft pseudopotential parameter were self-consistently calculated with the use of the condition of minimum free energy and with agreement of the theoretical and empirical values of electrical resistance. The positions of the first two maximums of the structure factor were calculated. Satisfactory agreement was obtained between calculated and empirical results.

The appearance of thermodynamic perturbation theories was accompanied by the elaboration of methods to calculate the structure and thermodynamic properties of liquid metals and alloys. A hard-sphere liquid is chosen as the comparison system in these theories, and the difference between the actual and hard-sphere potential is regarded as a perturbation.

We will represent the complete interaction potential  $\Phi$  in the form [1]

$$\Phi = \Phi_0 + \Phi_1, \quad (1)$$

where  $\Phi_0$  is the hard-sphere potential,  $\Phi_1$  is the potential corresponding to the perturbation. Here, the Helmholtz free energy of the liquid metal  $F$  satisfies the Gibbs-Bogolyubov inequality

$$F \leq F_0 + \langle \Phi_1 \rangle_0, \quad (2)$$

where  $F_0$  is the free energy of a system of hard spheres;  $\langle \Phi_1 \rangle_0$  is the configurational averaging of the perturbing potential for the hard-sphere system.

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