HETEROLYTIC DISSOCIATION OF SODIUM CHROMATE IN THE GAS PHASE AND ENTHALPY OF THE FORMATION OF $NaCrO_4^-$

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In this work, the method of ion-molecular equilibria has been used to investigate negative ions in saturated sodium chromate vapor. The mass spectrum of the negative ions has been recorded. The $Na_2CrO_4-Na_2SO_4$ system has been investigated. The enthalpy of formation of the $NaCrO_4^-$ ion $\Delta_f H_0^0 (NaCrO_4) = 968$ kJ/mole and the energy of heterolytic dissociation

$D_0^0 (Na^+ - NaCrO_4^-) = 625$ kJ/mole have been determined. The values obtained agree well with literature figures.

Since 1978, investigations of negative ions in vapors of salts of inorganic compounds at high temperatures have been carried on. Various negative ions have been recorded (for example,

$$AlF_4^-, Al_2F_7^-, KAl_2F_8^-, OH^-, KOH^-, PO_2^-, PO_3^-$$
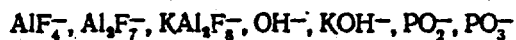
and others), their enthalpies of formation have been determined, and their electron affinities have been calculated [1-4].

Particular interest is being aroused by negative ions of the type of KSO_4^- [5], $KCrO_4^-$ [6], and $NaSO_4^-$ [7]. The determination of their enthalpies of formation permitted the calculation of the energies of heterolytic dissociation (U_{hd}) for the corresponding salts of dibasic acids to the first degree
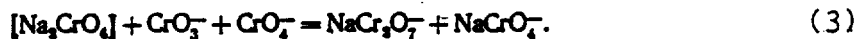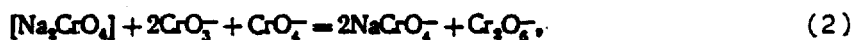
$$M_2XO_4 = M^+ + MXO_4^-.$$

The value of U_{hd} found can be called the experimental value, since it is determined unambiguously from the results of investigations. At the same time, to describe gas-phase molecules of the type of M_2XO_4 various ionic potential functions have been proposed hitherto [8,9], on the basis of which it is possible to carry out a theoretical calculation of the energy of heterolytic dissociation. Comparison of the theoretical and experimental values of U_{hd} enables the validity of the use of these ionic potential functions to be established [10].

The aim of the present work was to investigate negative ions in saturated

sodium chromate vapor, to determine the enthalpy of formation of the $NaCrO_4^-$ ion, and to calculate the energy of heterolytic dissociation of sodium chromate to the first stage.

The sodium chromate was synthesized from sodium dichromate. The quality of the material obtained was checked by X-ray phase analysis. This work was performed on a MKh-1303 mass spectrometer adapted for the study of ion-molecule equilibria (a combination of a Knudsen diffusion chamber with the mass-spectral recording of the charged components of the vapor), [1,5]. A platinum crucible with a ratio of the evaporation area to the diffusion area of ≈ 150 was used. In the course of the experiment, only the negative ions were measured and the neutral components of the vapor were not recorded.

The evaporation of the pure sodium chromate was performed in the temperature interval of 1170-1280 K. The mass spectra of the negative ions $CrO_3^-(1000)$, $CrO_4^-(1,9)$, $NaCrO_4^-(6,5)$, $Cr_2O_6^-(1,6)$, $NaCr_2O_7^-(1,9)$, $Na_3Cr_2O_6^-$ (2,0) were recorded; the ion currents in relative units at 1255 K are given in parentheses. The equilibrium constants of the following reactions were calculated from the measured ion currents:

$$[Na_2CrO_4] + NaCrO_4^- = Na_3Cr_2O_8^-, \tag{1}$$

$$[Na_2CrO_4] + 2CrO_3^- + CrO_4^- = 2NaCrO_4^- + Cr_2O_6^-, \tag{2}$$

$$[Na_2CrO_4] + CrO_3^- + CrO_4^- = NaCr_2O_7^- + NaCrO_4^-. \tag{3}$$

Square brackets indicate that the substance is present in the condensed state. For the pure chromate, the activity was considered to be equal to unity. The ratio of the partial pressures of the ions were calculated from the measured ion currents [1]:

$$\frac{P(A^-)}{P(B^-)} = \frac{I(A^-)M(A^-)i(B^-)}{I(B^-)M(B^-)i(A^-)},$$

where I is the measured ion current, at the electron multiplier, M is the molecular weight, and i is the amount of the isotope measured.

The temperature dependences of the equilibrium constants (1)-(3) were approximated by straight lines in the coordinates ln K versus $1/T$:

$$\ln K(1) = -443/T - 0,072,$$
$$\ln K(2) = 7260/T - 14,3,$$
$$\ln K(3) = 3420/T - 6,41.$$

The error of the approximating equations obtained as a function of the temperature can be evaluated from the formula

$$s(\ln K) = 0,31 \left[\frac{1}{30} + 6,5 \cdot 10^7 \left(\frac{1}{T} - \frac{1}{1237} \right)^2 \right]^{1/2}.$$

To determine the enthalpy of formation of the $NaCrO_4^-$ ion the Na_2CrO_4-Na_2SO_4 system was investigated (two compositions: 50 and 80 mol.% of Na_2SO_4). The following negative ions were recorded: SO_2^- (0,04), SO_3^- (0,19), $NaSO_4^-$ (0,25), $Na_3S_2O_8^-$ (0,012), CrO_3^- (1000), CrO_4^- (1,6), $NaCrO_4^-$ (4,53), $Cr_2O_6^-$ (1,08), $NaCr_2O_7^-$ (1,1), $Na_3Cr_2O_8^-$ (0,79), $Na_3CrSO_8^-$ (0,1

Table 1

Equilibrium Constants of Reactions (4)-(6)

Experiment No.	T (K)	$\ln K$ (4)	s_i^c	n_i^d	$\ln K$ (5)	s_i	n_i	$\ln K$ (6)	s_i	n_i
I[a]	1344	2,32	0,30	2	5,65	0,10	2	—8,03	0,05	2
	1387	2,43	0,10	3	5,61	—	1	—7,61	—	1
	1480	2,70	0,37	2	5,39	—	1	—7,78	—	1
	1344	2,96	0,44	2	5,14	—	1	—8,22	—	1
	1387	3,08	0,16	2	5,21	—	1	—7,81	—	1
II[b]	1300	3,00	0,27	6	5,29	0,06	3	—7,44	0,05	3
	1335	2,58	0,20	6	5,21	0,08	3	—7,57	0,03	3
	1385	2,54	0,14	7	5,07	0,20	4	—7,11	0,19	4

a) 50 mol.% of sodium sulfate; b) 80 mol.% of sodium sulfate; c) s_i is the standard deviation of the relative measurement; d) is the number of measurements of the equilibrium constant at the given temperature.
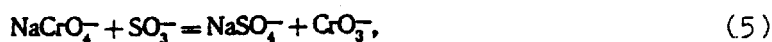
Table 2

Activities of the Components in the Na_2SO_4-Na_2CrO_4 System

No.	Concentration	T, K	a (Na_2CrO_4)						a (Na_2SO_4)	
			(1)[a]	n[b]	(2)	n	(3)	n	(7)	n
I	50 mol.%	1344	0,63	2	0,53	2	0,52	2	0,24	2
		1387	0,54	2	0,57	1	0,50	1	0,24	3
		1490	0,74	2	0,90	1	0,65	1	0,42	2
		1344	0,64	2	0,80	1	0,79	1	0,47	2
		1387	0,66	2	0,94	1	0,76	1	0,52	2
II	80 mol.%	1300	0,13	6	0,09	3	0,10	3.	0,94	6
		1335	0,15	6	0,12	3	0,14	3	0,96	6
		1385	0,12	7	0,15	4	0,13	4	0,82	7

a) Numbers of the reactions from the equilibrium constants of which the activities were calculated are given in parentheses; b) n is the number of measurements.

ion currents and relative units recorded for the composition with 50 mol.% of Na_2SO_4 are given in parentheses.

From the measured ion currents we calculated the equilibrium constants of reaction (Table 1)

$$[Na_2CrO_4] + NaSO_4^- = [Na_2SO_4] + NaCrO_4^-, \qquad (4)$$

$$NaCrO_4^- + SO_3^- = NaSO_4^- + CrO_3^-, \qquad (5)$$

$$SO_3^- + CrO_3^- = CrO_4^- + SO_2^-. \qquad (6)$$

Let us dwell in more detail on reaction (4). To calculate the equilibrium

Table 3

Enthalpies of Reactions (4)–(6) (kJ/mole)

Experiment No.	ΔH_0^0 (4)	ΔH_0^0 (5)	ΔH_0^0 (6)
I[a]	—37,8±5,5	—72,6±3,3	91,2±3,3
II[a]	—37,1±4,7	—68,2±1,8	83,0±3,2
Recommended[b]	—37±15	—70±18	88±14

[a] The standard deviation of an individual measurement is given; [b] the total error including the error of the thermodynamic functions of the participants is given.

constant:

$$K(4) = \frac{P(NaCrO_4^-)}{P(NaSO_4^-)} \cdot \frac{a(Na_2SO_4)}{a(Na_2CrO_4)}$$

The activities of the components in the Na_2SO_4–Na_2CrO_4 system are required. The activity of sodium chromate was determined via the ion-molecule reaction (1) from the equation

$$a(Na_2CrO_4) = \frac{P(Na_2Cr_2O_8^-)}{P(NaCrO_4^-)} \cdot \frac{1}{K(1)}$$

The activity of sodium chromate was determined similarly from reactions (2) and (3). The values obtained agreed well with one another (Table 2).

The activity of sodium sulfate was calculated from the ratio of the ion currents of $Na_3S_2O_8^-$ and $NaSO_4^-$

$$a(Na_2SO_4) = \frac{P(Na_3S_2O_8^-)}{P(NaSO_4^-)} \cdot \frac{1}{K(7)}$$

where K(7) is the equilibrium constant of the ion-molecule reaction

$$[Na_2SO_4] + NaSO_4^- = Na_3S_2O_8^- \qquad (7)$$
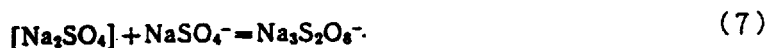
To determine the numerical values of K(7), pure sodium sulfate was evaporated. The following negative ions were recorded: SO_2^- (3,8), SO_3^- (100), SO_4^- (16,7), $NaSO_4^-$ (33), $Na_3S_2O_8^-$ (7,1). The mass spectrum at 1387 K is given. In the temperature interval of 1255–1473 K the values obtained are approximated by the straight line:

$$\ln K(7) = 1285/T - 1,67.$$

The error of this equation as a function of the temperature was evaluated from the formula:

$$s[\ln K(7)] = 0,23 \left[\frac{1}{107} + 8,9 \cdot 10^6 \left(\frac{1}{T} - \frac{1}{1373} \right)^2 \right]^{1/2}.$$

Table 4

Supplementary Thermodynamic Information

Compound	$\Delta_f H_0^0$, kJ/mole	Reference	$\phi_{1200^\circ}^0$	$\phi_{1400^\circ}^0$	$\Delta\phi$,	Reference
				J/mole·K		
Na_2SO_4, s	—1376,4±0,4	[11]	·246,8	275,7	±1,5	[11]
Na_2CrO_4, s	—1335,2±3,3	[12]	271,9	301,4	±2,5	[13]
$NaSO_4^-$	—972±12	[7]	367,8	383,6	±7,3	[7]
SO_2^-	—400,1±3,5	[11]	277,3	285,4	±3,0	[11]
SO_3^-	—601,1±7,4	[5]	299,4	309,3	±3,7	[5]
CrO_3^-	—674±27	[6]	311,5	322,1	±4,0	[11]
CrO_4^-	—785±30	[6]	333,6	346,5	±5,8	[6]
$NaCrO_4^-$	—968±18	our work	387,4	404,1	±8,1	[13]

The enthalpies of reactions (4)-(6) were calculated from the third law of thermodynamics (Table 3). The necessary thermodynamic functions of the partial reactions were taken from the literature (Table 4). The enthalpies of the reactions determined from the results of two experiments with different compositions of the system agreed satisfactorily with one another. The mean values of the enthalpies of the reactions are taken as the recommended figures.

From the enthalpy of reaction (4) we calculated $\Delta_f H_0^0(NaCrO_4^-) = —968±18$ kJ/mole and the energy of the heterolytic dissociation of sodium chromate to the first stage $D(Na^+—NaCrO_4^-) = 625$ kJ/mole, $(\Delta_f H_0^0(Na_2CrO_4, r) = —990$ kJ/mole [14], $\Delta_f H_0^0(Na^+) = 603,6$ kJ/mole. This value can be compared with values obtained previously $D(K^+—KCrO_4^-) = 578$, $D(Na^+—NaSO_4^-) = 658$, $D(K^+—KSO_4^-) = 599$ kJ/mole [7]. All the figures correlate well with one another.

In conclusion, we may note that good agreement of these thermodynamic magnitudes obtained in this work and those given in the literature. The value of the enthalpy of formation of $NaCrO_4^-$ obtained in the work and the enthalpies of formation of $NaSO_4^-$, CrO_3^-, and SO_3^- given in Table 4 permit the calculation $\Delta H_0^0(5) = —73±25$ kJ/mole. The calculated value is in good agreement with the value found experimentally of $\Delta H_0^0(5) = —70±18$ kJ/mole. The enthalpy of the reaction $\Delta H_0^0(6) = —88±14$ kJ/mole also agrees well with the literature figure of $\Delta H_0^0(6) = 91±11$ kJ/mole [7].

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