Phase Diagram for the System $Na_2Cr_2O_7 + NaNO_3 + H_2O$ in the Temperature Range 20 °C to 40 °C

Eli Korin* and Leonid Soifer

Department of Chemical Engineering, Ben-Gurion University of the Negev, P.O. Box 653, Beer-Sheva 84105, Israel

The phase diagram for the ternary system $Na_2Cr_2O_7 + NaNO_3 + H_2O$ was determined at three temperatures, (20, 30, and 40) °C. In addition, the densities of the saturated aqueous solutions were measured. The experimental results show that in the temperature range (20 to 40) °C, only anhydrous sodium nitrate and sodium dichromate dihydrate were present as solid phases.

Introduction

Conventional quantitative analysis of Cr_2O_3 is based on the decomposition of Cr_2O_3 by a chemical reaction between sodium or potassium nitrate and a molten sample of the oxide (Remy, 1961). The product of this reaction is sodium or potassium dichromate, which is highly soluble in water. This enables simple separation of the chromate from the original sample. This process is currently being applied for the separation of Cr_2O_3 from the ash obtained by burning chrome ores (Sen Supta and Chattergree, 1992). In order to exploit this application to the full, it is necessary to have comprehensive data on the solubilities of the dichromate salts in water under different conditions. Solubility data for the following binary systems are available in the literature: $K_2Cr_2O_7 + H_2O$, $Na_2Cr_2O_7 + H_2O$, in the temperature range (20 to 40) °C (Sohnel and Novotny, 1985); $KNO_3 + H_2O$, in the temperature range (20 to 40) °C (Seidell, 1965); and $NaNO_3 + H_2O$, in the temperature range (−18 to +317) °C (Seidell, 1965). For the ternary system $K_2Cr_2O_7 + KNO_3 + H_2O$, only the compositions at the invariant points at (20, 30, and 40) °C have been reported (Seidell, 1965). There are no data on the ternary system $Na_2Cr_2O_7 + NaNO_3 + H_2O$.

The purpose of this work was thus to determine experimentally the phase diagram of the ternary system $Na_2Cr_2O_7 + NaNO_3 + H_2O$ at three temperatures, (20, 30, and 40) °C, and to measure the density of the saturated aqueous solution. The results may be used to optimize the analytical method for Cr_2O_3 and to improve the separation process of Cr_2O_3 from solid industrial wastes.

Experimental Section

Materials. Extra-pure sodium nitrate (DABG E251, 99.0%), sodium dichromate (99.5%), and Mohr's salt [extrapure $(NH_4)_2(FeSO_4)_2 \cdot 6H_2O$, ±2%] were supplied by Merck. Deionized water was obtained by means of a Modulab Mode Pure Plus system (Continental Water System Corp.).

Apparatus. A schematic description of the experimental apparatus is given in Figure 1. The experiments were performed in a 0.5-dm^3 glass beaker (B), which was closed by a cover (S) and immersed in a water bath (A) whose temperature was controlled by an electrical thermostat (Haake Corp). The mixture was stirred continuously with a stirrer (D). The temperatures in the flask and in the water bath were measured by copper−constantan thermocouples (±0.2 °C), which were calibrated by thermometer model Lauda R 42 (±0.01 °C). Samples were withdrawn by a special sampling system, as follows. The aqueous samples were sucked through a porous glass filter (F) into a sampling glass container (C) by means of a vacuum pump. The sampling system was heated to slightly more than the saturation temperature to prevent possible crystallization. Heating was accomplished by means of a heating jacket (J), in which hot water was circulated from the thermostatic bath. The system was left unstirred for 15 min before sampling to enable all the suspended crystals to settle. Sampling lasted about 2 s.

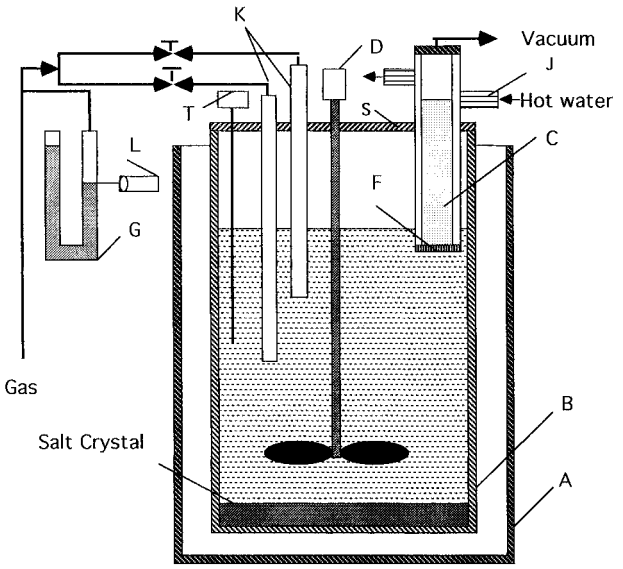

Figure 1. Schematic description of the apparatus for solubility measurement: (A) thermostated water bath; (B) glass beaker (0.5 dm^3); (C) sampling system; (D) stirrer; (F) glass filter; (G) micromanometer; (J) heating jacket; (K) glass tubing; (L) cathetometer; (S) cover; (T) thermocouple.

At each temperature, the experiments were run according to the following procedure: (a) To determine the equilibrium solubility curve of sodium dichromate dihydrate, weighed amounts of saturated solutions of sodium chromate dihydrate at the temperature of the experiment were mixed with a weighed amount of sodium nitrate crystals, which caused salting out of the sodium chromate dihydrate. (b) To determine the equilibrium curve of sodium nitrate solubility, weighed amounts of saturated solutions of sodium nitrate at the temperature of the experiment were mixed with a weighed amount of sodium dichromate dihydrate crystals to facilitate salting out of the sodium nitrate. (c) To reach the invariant point, saturated solutions of sodium dichromate dihydrate and

* To whom correspondence should be addressed. E-mail: ekorin@bgumail.bgu.ac.il.

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Table 1. Densites (ρ/kg·dm^{-3}) of Pure Liquids and Binary Solutions

substance	t/°C	this work	lit. data: Sohnel and Novotny (1985)	lit. data: Weast and Lide (1989−1990)
water	20	0.999		0.998
glycerol	20	1.260		1.263
ethyl alcohol	20	0.798		0.797
NaCl (4.1 wt %) + water	20	1.030		1.029
saturated solution of KCl in water	30	1.181	1.181	
saturated solution of $NaNO_3$ in water	20	1.75	1.381	
	30	1.406	1.396	
	40	1.411	1.412	
	60	1.431	1.443	
saturated solution of $Na_2Cr_2O_7$ in water	20	1.740	1.615	
	30	1.756	1.630	
	40	1.778	1.649	

Table 2. Comparison of Solubility Data Measured in This Work with Literature Data

system	t/°C	solubility (kg/100 kg of mixture): this work	solubility (kg/100 kg of mixture): Sohnel and Novotny (1985)
+ H_2O	40	26.9	27.11
Cr_2O_7 + H_2O	20	64.0	64.43
Cr_2O_7 + H_2O	30	66.0	66.08
Cr_2O_7 + H_2O	40	68.7	67.98
$NaNO_3$ + H_2O	20	46.9	46.58
$NaNO_3$ + H_2O	30	47.8	48.78
$NaNO_3$ + H_2O	40	51.1	50.97
$NaNO_3$ + H_2O	60	55.4	55.32

Table 3. Solubility Data for the Ternary System Cr_2O_7 + $NaNO_3$ + H_2O at 20 °C

concn (kg of anhydrous salt/100 kg of H_2O): $NaNO_3$	concn (kg of anhydrous salt/100 kg of H_2O): $Na_2Cr_2O_7$	solid phase	ρ/kg·dm^{-3}
88.4	00.0	$NaNO_3$	1.375
69.6	28.1	$NaNO_3$	1.442
58.5	44.2	$NaNO_3$	1.463
45.8	65.2	$NaNO_3$	1.520
40.2	76.3	$Na_2Cr_2O_7$·$2H_2O$ + $NaNO_3$	1.542
38.5	74.3	$Na_2Cr_2O_7$·$2H_2O$	1.557
39.4	83.0	$Na_2Cr_2O_7$·$2H_2O$	1.564
21.4	119.7	$Na_2Cr_2O_7$·$2H_2O$	1.655
9.2	151.2	$Na_2Cr_2O_7$·$2H_2O$	1.691
00.0	177.8	$Na_2Cr_2O_7$·$2H_2O$	1.740

sodium nitrate were mixed to obtain salting out of both sodium nitrate and sodium dichromate dihydrate. In addition, to check the method, some experiments were also performed to reach equilibrium by an alternative path, starting with unsaturated solutions of one of the salts and mixing it with an excess amount of crystals of the second

To ensure that sampling was performed at equilibrium conditions, a preliminary test was carried out in which the liquid concentration and the density were measured as a function of time. Two types of experiment were carried out, one starting from a supersaturated solution, in which the solid phase precipitated to reach equilibrium and the other, starting from a nonsaturated solution, in which solid dissolved to reach equilibrium. The results showed that for both cases about 3 h was sufficient to reach equilibrium. In our experiments, sampling was performed after a minimum of 5 h.

The compositions of the solid phases were determined by Schreinemaker's method (Schreinemakers, 1907; quoted in Mullin, 1993). In addition, for the invariant points and for at least one point on each saturation curve, the solid

Table 4. Solubility Data for the Ternary System $Na_2Cr_2O_7$ + $NaNO_3$ + H_2O at 30 °C

concn (kg of anhydrous salt/100 kg of H_2O): $NaNO_3$	concn (kg of anhydrous salt/100 kg of H_2O): $Na_2Cr_2O_7$	solid phase	ρ/kg·cm^{-3}
91.7	00.0	$NaNO_3$	1.406
89.4	4.0	$NaNO_3$	1.416
85.9	13.8	$NaNO_3$	1.435
63.8	47.7	$NaNO_3$	1.436
55.7	57.3	$NaNO_3$	1.435
47.8	72.8	$NaNO_3$	1.446
47.1	77.0	$Na_2Cr_2O_7$·$2H_2O$ + $NaNO_3$	1.472
43.4	89.7	$Na_2Cr_2O_7$·$2H_2O$	1.502
36.1	106.4	$Na_2Cr_2O_7$·$2H_2O$	1.519
30.0	143.5	$Na_2Cr_2O_7$·$2H_2O$	1.650
20.8	150.4	$Na_2Cr_2O_7$·$2H_2O$	1.710
11.3	181.0	$Na_2Cr_2O_7$·$2H_2O$	1.737
00.0	194.3	$Na_2Cr_2O_7$·$2H_2O$	1.756

Table 5. Solubility Data for the Ternary System $Na_2Cr_2O_7$ + $NaNO_3$ + H_2O at 40 °C

concn (kg of anhydrous salt/100 kg of H_2O): $NaNO_3$	concn (kg of anhydrous salt/100 kg of H_2O): $Na_2Cr_2O_7$	solid phase	ρ/kg·cm^{-3}
104.6	00.0	$NaNO_3$	1.411
93.3	33.2	$NaNO_3$	1.463
89.0	58.2	$NaNO_3$	1.500
86.9	58.3	$NaNO_3$	1.505
83.9	61.8	$NaNO_3$	1.507
68.8	67.7	$NaNO_3$	1.505
62.0	69.4	$NaNO_3$	1.503
50.8	75.2	$Na_2Cr_2O_7$·$2H_2O$ + $NaNO_3$	1.510
45.0	100.4	$Na_2Cr_2O_7$·$2H_2O$	1.653
41.7	133.0	$Na_2Cr_2O_7$·$2H_2O$	1.684
38.3	128.7	$Na_2Cr_2O_7$·$2H_2O$	1.680
35.5	152.7	$Na_2Cr_2O_7$·$2H_2O$	1.752
15.0	197.5	$Na_2Cr_2O_7$·$2H_2O$	1.772
14.2	192.0	$Na_2Cr_2O_7$·$2H_2O$	1.768
00.0	220.0	$Na_2Cr_2O_7$·$2H_2O$	1.778

phases were identified by X-ray analysis using a PW 1050/70 Philips X-ray diffractometer.

The density of the aqueous solutions was determined by the method of maximum bubble pressure using air as the bubble gas (Rapp, 1970). This on-line measurement method provides a convenient way to determine the density of saturated solutions. The differences in the manometer level were measured with a cathetometer to an accuracy of ±0.01 mm (W. G. Pye and Co. Ltd., Cambridge, England). The method was calibrated against values obtained with a pycnometer and evaluated with respect to literature data for pure substances: water, glycerol and ethyl alcohol (Weast, 1989−1990). In addition, our results were compared to literature data for aqueous solutions of sodium chloride and saturated solutions of potassium chloride, sodium nitrate, and sodium dichromate (Table 2). The accuracy of our method is ±0.1% and the reproducibility is ±0.5%.

Analytical Methods. The concentrations of Cr_2O_3 were determined by titration against Mohr's salt (Furman, 1968). About 8 g of sample solution was used. The precision of the method is ±0.5%, and the reproducibility is ±0.3%. The water content was determined by evaporating weighed samples of about 8 g in an oven at 150 °C for 12 h, precision ±0.2% and the reproducibility ±0.1%. The concentration of sodium nitrate was determined by mass balance calculation, using eq 1 where X_n and X_c are the

$$X_n = \frac{m_s(1 - X_c) - m_w}{m_s} \quad (1)$$

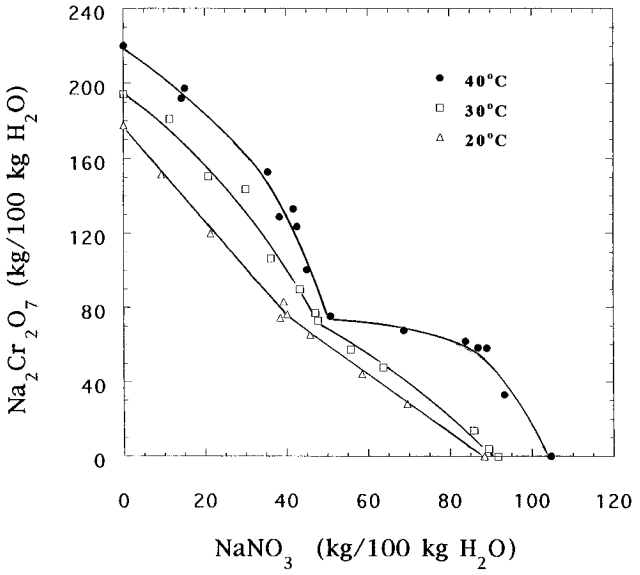

Figure 2. Phase diagram of the ternary system $Na_2Cr_2O_7$ + $NaNO_3$ + H_2O at (20, 30, and 40) °C.

concentrations (kg of anhydrous salt/100 kg of solution) of $NaNO_3$ and $Na_2Cr_2O_7$, respectively, m_s is the total mass of the sample solution in kg, and m_w is the mass of water in the sample.

Results and Discussion

In order to check the reliability of our experimental system, we first measured the solubilities of $Na_2Cr_2O_7 \cdot 2H_2O$ and $NaNO_3$ in water and the densities of the saturated aqueous solutions and compared the results to values in the literature (Tables 1 and 2). For the measurements of the densities of saturated $Na_2Cr_2O_7 \cdot 2H_2O$ solutions (Table 1), our results were identical to those given by Sohnel and Novotny (1985). For saturated $NaNO_3$ solutions the difference was less than 0.8%. The values in Table 2 show that the differences between our solubility data and literature values fall within the range of the experimental error of the analytical methods.

The experimental results for the ternary system $Na_2Cr_2O_7$ + $NaNO_3$ + H_2O at (20, 30, and 40) °C are given in Tables 3−5, respectively. The results show that in a temperature range of (20 to 40) °C, only anhydrous sodium nitrate and sodium dichromate dihydrate exist as solid phases. The isotherms for the three cases are presented in Figure 2.

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Symbols

X_n	concentration of $NaNO_3$
X_c	concentration of $Na_2Cr_2O_7$
m_s	total mass of sample solution
m_w	mass of water in sample solution
ρ	density
t	temperature

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