

A mixture of 15 g. of the picrate and 100 ml. of 5% sodium hydroxide was refluxed for 5 hours. The mixture was cooled and extracted with ether. A brown oil (7.8 g., 84% based on the amount of picrate used) was obtained, which solidified on standing (m.p. 32–38°). One recrystallization from absolute ethanol gave 6.2 g. (67%) of product, m.p. 34–36°. Further recrystallization did not improve the melting point.

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The Solubility and Transition Point of Lithium Chromate

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Data reported by earlier workers for the solubility of lithium chromate at 18,¹ 20² and 30³ are not consistent. Further, while the usual composition of the salt is the dihydrate, our observations confirm the findings of Retgers⁴ that an anhydrous salt separates from the aqueous solution on boiling. It therefore seemed desirable to determine the solubility over the range 0 to 100°, and the temperature of transition between the dihydrate and the anhydrous salt.

Experimental

The material used for the solubility experiments was recrystallized $\text{Li}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$, prepared from lithium hydroxide monohydrate and chromic anhydride. It was found to contain 99.85% $\text{Li}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$ based on its hexavalent chromium content, 0.006% Cl and 0.021% SO_4 . It was necessary to remove traces of trivalent chromium and insoluble matter from the solutions before the final crystallization; this was done by oxidation with a small amount of sodium hypochlorite and filtrations. The final product consisted of bright yellow crystals. Solubility⁵ and transition point⁶ were determined by previously described methods. The following results were obtained:

Temp., °C.	Solubility, wt. % Li_2CrO_4	Solid phase
0.7	47.27	$\text{Li}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$
7.2	47.74	$\text{Li}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$
10.4	47.89	$\text{Li}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$
20.0	48.60	$\text{Li}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$
29.8	49.62	$\text{Li}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$
40.2	50.66	$\text{Li}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$
50.1	52.10	$\text{Li}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$
60.0	53.52	$\text{Li}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$
70.0	55.27	$\text{Li}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$
74.6		$\text{Li}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O} + \text{Li}_2\text{CrO}_4$
75.1	56.17	Li_2CrO_4
80.0	56.34	Li_2CrO_4
90.0	56.57	Li_2CrO_4
100.0	56.82	Li_2CrO_4

The values when plotted yield smooth curves. For the dihydrate, the equation

$$S = 47.25 + 0.05037T + 0.0009143T^2$$

fits the observed data with an average deviation of 0.05%

(1) F. Mylius and R. Funk, *Abh. phys.-chem. Reichsanstalt*, **3**, 456 (1900).

(2) P. P. von Weimarn, *Z. Chem. Ind. Kolloide*, **9**, 25 (1911).

(3) F. A. H. Schreinemakers, *Z. physik. Chem.*, **58**, 77 (1906).

(4) J. W. Retgers, *ibid.*, **3**, 53 (1891).

(5) W. H. Hartford and K. A. Lane, *THIS JOURNAL*, **70**, 647 (1948).

(6) W. H. Hartford, K. A. Lane and W. A. Meyer, Jr., *ibid.*, **72**, 3353 (1950).

and a maximum deviation of 0.09%. For the anhydrous salt, the equation

$$S = 52.646 + 0.06265T - 0.0002096T^2$$

fits the data with an average deviation of 0.01% and a maximum deviation of 0.02%. Calculation of the concentration at the transition temperature gives: from the dihydrate equation, 56.10% Li_2CrO_4 ; from the anhydrous salt equation, 56.15% Li_2CrO_4 .

A value of 56.12% Li_2CrO_4 is therefore reported for the solution concentration in equilibrium with the two solid phases at the transition temperature of 74.6°.

As might be expected from the relatively slight change of solubility of both phases with temperature and the oblique angle of intersection of the two solubility curves, the heat effect on transition is very small, and is estimated to be of the order of 1–2 kcal./mole, as contrasted with 15 kcal./mole reported⁷ for the $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{CrO}_4 \cdot 6\text{H}_2\text{O}$ transition. It was necessary to heat and cool at rates in the order of 0.01°/minute to detect the thermal breaks, which were obtained at 74.6° on both heating and cooling.

Of the previous solubility determinations, only that of Schreinemakers,³ who reported 49.94% Li_2CrO_4 at 30°, is in agreement with the present work.

An attempt was made to determine the temperature of the ice-dihydrate eutectic. This proved to be below –60°; equipment and measuring facilities were not available to investigate lower temperatures.

An unusual characteristic of the anhydrous salt is its ready solubility in the lower alcohols. Sodium chromate is soluble to the extent of only 0.35%⁸ in methanol and even less in ethanol at room temperature. Other anhydrous chromates are virtually insoluble in alcohols. Anhydrous lithium chromate was prepared for study by slowly boiling a saturated solution of the dihydrate. The yellow crystals were 99.83% Li_2CrO_4 . An approximate determination of the solubility of the salt in commercial absolute methanol and ethanol was made by rotating sealed containers containing these compounds with an excess of lithium chromate in a constant temperature bath for eight hours. The bottles were protected from light by a covering of black tape, since alcoholic solutions of lithium chromate, although stable for more than two months in the dark, were found to undergo decomposition fairly rapidly, with deposition of hydrous chromic chromate, when exposed to light. The following results were obtained:

Temp., °C.	Solubility, wt. % Li_2CrO_4	
	Methanol	Ethanol
0.5	13.4	1.6
24.4	15.7	1.8

The dihydrate is somewhat more soluble than the anhydrous salt, but its true solubility in alcohols cannot be determined, since the salt is dehydrated by these solvents.

Anhydrous lithium chromate was found to be insoluble in ether, and soluble only to the extent of about 25 p.p.m., as judged by color, in acetone. The low solubility in acetone explains the previously reported⁹ decomposition of lithium dichromate to lithium chromate in acetone solution.

Density of the dihydrate and the anhydrous salt was determined by immersion in toluene in a pycnometer: Li_2CrO_4 , d_{25}^{25} , 2.426; $\text{Li}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$, d_{25}^{25} , 2.149.

(7) Natl. Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Washington, D. C., 1949, p. II, 92–96.

(8) This value is from unpublished data by E. A. Roche of this Laboratory.

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The Reaction of Silver *n*-Perfluorobutyrate with *n*-Perfluoropropyl Iodide and with 1,2-Dibromo-1-chlorotrifluoroethane

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Several attempts were made to synthesize perfluorinated esters by the reaction of silver salts of