

the pH being between 1 and 2. The tests against the malarial parasite are not completed.

Summary

The hydrochlorides of a series of alkyl N-(8-quinoly) carbamates in which the alkyl group

was varied from methyl to *n*-hexyl were prepared and tested for their local anesthetic activity. The methyl and ethyl derivatives produced local anesthesia for a short time. All the compounds were irritating.

URBANA, ILLINOIS

RECEIVED JUNE 15, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE OF THE COLLEGE OF THE CITY OF NEW YORK]

The Binary System Potassium Dichromate-Sodium Dichromate

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The literature lists no determination of the liquidus curve of the system potassium dichromate-sodium dichromate. These are two fairly stable compounds having low melting points as compared with most salts and there existed the possibility of a low temperature eutectic mixture which could be used as a bath liquid. Furthermore as potassium dichromate has a transition point at about 240° the system offered the possibility of detecting the formation of solid solution by a change in the transition point due to solid solution. Still further the melting point of sodium dichromate is recorded in the literature on the basis of a determination made in 1886.¹ The report of this early work does not state the method of purification of the salt, nor the method of determining the melting temperature. It was thought advisable to measure it with more modern instruments.

In the work being reported the points on the liquidus curve were determined by two methods. The first was that of thermal analysis using copper-constantan couples and a potentiometer. The second was that of observing the temperature on a thermometer when crystallization of a homogeneous melt started or when the last crystal of a previously melted and solidified mix disappeared. The melting point of sodium dichromate and the transition point of potassium dichromate were determined by thermal analysis using time-temperature and time-differential temperature curves.

Experimental

Materials.—The potassium dichromate was twice recrystallized from a filtered solution of the c. p. salt and then fused in an electric furnace which was kept just above the melting point of potassium dichromate. As potassium dichromate expands on passing through its transition

point the tube containing the molten salt was tilted before solidification to an almost horizontal position to prevent cracking of the tube when the expansion took place. On changing crystal form and expanding, the solid mass disintegrates and was poured from the tube as a coarse powder. In separating the crystals from the mother liquid and in subsequent handling care was taken to avoid contact with organic material.

Sodium dichromate was prepared from c. p. hydrated salt by recrystallizing twice after rejecting the first crop of crystals.² The recrystallized hydrate was kept in a porcelain dish at 170° for eight hours in which time it was converted to the anhydrous salt. It was then fused in Pyrex tubes set in a furnace which was maintained at a temperature just above the melting point. The molten salt was poured into a porcelain dish and the resulting solid ground to a powder and kept over phosphorus pentoxide.

The mixtures were made by weighing by difference, the weights being taken to the nearest centigram. The salts were poured from the weighing tubes directly into the Pyrex test-tubes used for the determinations.

Apparatus.—The apparatus for thermal analysis consisted of a cylinder of electrolytic copper 7.6 cm. in diameter and 12.7 cm. high, having three drilled wells. Two of the wells held Pyrex test-tubes 2.5 × 20 cm., one of which contained the dichromates and the other shredded asbestos. A thin layer of asbestos paper surrounded the test-tubes and ensured a small temperature difference between the salt and the copper block when the temperature of the block was changing. The third well, much smaller in diameter, held a chromel-alumel couple which was connected with a millivoltmeter graduated to read in degrees centigrade. This was used for the convenience of knowing the temperature of the copper block. The cylinder fitted snugly into a resistance furnace which was only slightly lagged. A rheostat and ammeter in series permitted control of the rate of heating and cooling.

The temperature measuring system consisted of two copper-constantan couples (24 gage wire) combined in the well-known way to allow a reading of the temperature of the sample, and of the difference in temperature between the sample and the shredded asbestos hereafter referred to as ΔT . Leeds and Northrup potentiometer indicators

(2) In connection with this see Nikitina, *Trans. Inst. Pure Reagents*, **9**, 161 (1930), and Richards and Kelley, *This Journal*, **33**, 847 (1911).

1) A. Stanley, *Chem. News*, **54**, 195 (1886).

were used to read the e. m. f. produced. A switch made it possible to read both the temperature and ΔT on the same instrument, but generally two potentiometers were used. A second switch reversed polarity in the ΔT circuit. All leads were of the same copper wire as used in the couples and the switches were protected from radiation from the furnace. The cold junction was cracked ice in an unsilvered Dewar flask. With these potentiometers the e. m. f. could be estimated to 0.01 mv. for temperatures up to 313°. For higher temperatures the scale allowed estimation only to 0.5 mv. It is our opinion that the error in reading the potentiometer was within 0.2° on the lower scale and within 0.5° on the higher one. The same potentiometer was always used for the temperature measurement. The couples were held in a shield of small bore Pyrex tubing.

Method.—The mixed salts in a Pyrex tube were inserted in the copper cylinder and the temperature raised to above the melting point. The couple in the guard tube was inserted into the melted salt, used to stir the liquid and then held in the center of the liquid by a cork stopper at the top of the tube. The rate of cooling of the copper cylinder was set as desired and readings taken every one-half or full minute of the temperature, and on alternate half or full minutes of ΔT when desired. The time- ΔT curve proved valuable in many cases, such as determining the transition point, and the eutectic temperature where the original mixture differed greatly from the eutectic mixture and the eutectic halt was of small duration.

The couple was calibrated against the boiling point of water, the melting point of Bureau of Standards tin and of twice crystallized potassium nitrate,³ and a curve of its deviation from the standard curve of Adams⁴ was prepared. The deviation curve was found to be a straight line and the melting point of potassium dichromate determined using this curve was 397.4°, which agrees with the value 397.5° found by Roberts.⁵ While the melting point of potassium dichromate is about 10° higher than the limit set for the copper-constantan couple by the standard tables, it was considered justifiable to extrapolate through this short range.

There was no stirring during the cooling of the melts and supercooling generally took place. To find the temperature at which crystallization would have started had supercooling not occurred, the cooling curve after crystallization had set in was extended back to its intersection with the cooling curve previous to crystallization. This point of intersection was taken as the initial crystallization point of the mix.

Sodium dichromate supercools much more than potassium dichromate. In one case pure sodium dichromate supercooled 40°. There was usually considerable supercooling at the eutectic point as well as at the temperature of initial crystallization, so much so in many cases that when crystallization of the second solid finally set in the temperature was so low that the heat of crystallization was insufficient to bring the temperature up to the eutectic point, and many of the runs resulted in useless curves. In the range between 15 and 45% of potassium dichromate it

was impossible to get a melting point without stirring. Even inoculation by dropping in a crystal of sodium dichromate did not help as the rate of solidification was too slow. The melting point of 22.9% potassium dichromate was obtained by using the guard tube and the couple as a stirrer.

The melted dichromates form a very dark liquid, impossible to see through to more than a few millimeters. Accordingly, for visual determinations of the temperature of initial crystallization, small Pyrex test-tubes were used as the containers and of course smaller charges. With the thermometer inserted the liquid in the annular space was short in depth and with good light the appearance or disappearance of the crystals could be observed. A thin glass rod was used to stir the mixture. The test-tube was suspended in a kerosene lamp chimney and the flame of a Tirril burner kept a short distance below the lower end of the chimney.

A nitrogen-filled mercury thermometer (5 to 500°) was used. It was calibrated in the apparatus for the depth of immersion used in the dichromate mixtures against the copper-constantan couple used in the other portion of this work. The temperature of the appearance and disappearance of the crystals could be found on repeated trials within a range of 2°. Due to the stirring there was practically no supercooling.

Results.—Five determinations of the melting point of sodium dichromate using different batches of the purified compounds gave the following values: 356.4, 356.6, 356.9, 356.4 and 357.2°; average 356.7°. The error all things included is probably within $\pm 1.0^\circ$. This value of the melting point of sodium dichromate is 36° higher than that obtained by Stanley¹ and chosen by the "I. C. T."⁶ Table I contains the results of measurements on the binary system obtained by thermal analysis, Table II contains those obtained by the visual method. The values are plotted in Fig. 1.

TABLE I
M. P. OF $K_2Cr_2O_7$ - $Na_2Cr_2O_7$ (BY THERMAL ANALYSIS)

% $K_2Cr_2O_7$:	M. p., °C.	Eutectic temp., °C.
100.0	397.4	...
84.7	373	304
69.1	351	304.6
57.9	328	304
53.2	317	303
37.9	...	304.6
26.9	...	306
24.9	...	304
22.9	315	304.6
14.6	335	...
0.0	356.7	...

The transition point of pure potassium dichromate was sharply shown by the ΔT and cooling curves. The cooling curve itself gave only a

(6) "I. C. T.," Vol. I, p. 152 (referred to in error as the m. p. of $Na_2Cr_2O_7 \cdot 2H_2O$).

(3) "I. C. T.," Vol. I, p. 155.

(4) "Pyrometric Practice," Bureau of Standards Technological Paper No. 170, p. 309.

(5) H. S. Roberts, *Phys. Rev.*, **23**, 386 (1924).

TABLE II
M. P. OF $K_2Cr_2O_7-Na_2Cr_2O_7$ (VISUAL METHOD-THERMOMETER)

% $K_2Cr_2O_7$	M. p., °C.	% $K_2Cr_2O_7$	M. p., °C.
85	372	45	311
72	351	37	303
61	333	29	310
50	316	21	320

slight inflection. This was to be expected, previous workers having shown the heat of transition to be quite small.^{7,10,11} Two determinations on different batches of purified potassium dichromate gave the values 241.3 and 242.0°; average, 241.6° with an error probably within $\pm 1.0^\circ$.

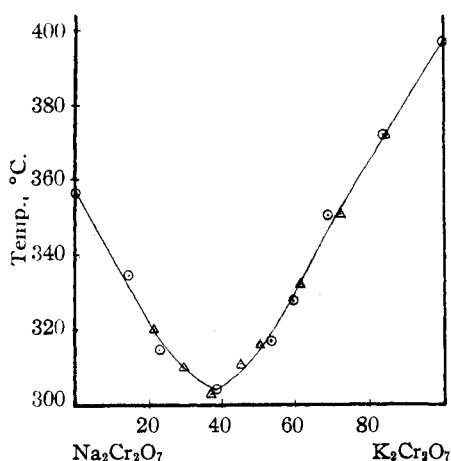


Fig. 1.—Liquidus of the $Na_2Cr_2O_7-K_2Cr_2O_7$ system: Δ , visual m. p.; \circ , m. p. by thermal analysis.

This value is higher than any recorded in the literature and about 5° higher than the value chosen by the "I. C. T."⁸ The most recent determination is that of Robinson, Stephenson and Briscoe.⁹ They found the transition point to be 236.8° using a platinum resistance thermometer and 241° using a mercury thermometer. Their paper does not state the method of calibrating the resistance thermometer, nor of the purification of the potassium dichromate. Earlier determinations are those of Schemtschuschny, trans. p. 236°,¹⁰ and Tammann, trans. p. 240°.¹¹

No mixture of potassium and sodium dichromates used in determining the liquidus curve gave any indication of passing through a transition

point between the eutectic temperature and room temperature. The ΔT curve showed no break and furthermore the solid masses formed around the thermocouple guard tube could be slid up and down the test-tubes after room temperature had been reached. When pure potassium dichromate was used the tube cracked due to expansion on passing through the transition. Robinson, Stephenson and Briscoe pointed out that the transition of potassium dichromate could be observed by dipping a rod into the molten salt, withdrawing the rod and letting it cool rapidly in the air.⁹ At the transition point the adhering salt changes color, swells and cracks into minute pieces which drop off leaving the rod clean. This phenomenon was used to find approximately the minimum concentration of sodium dichromate needed to prevent the transition of potassium dichromate. A 10% sodium dichromate on cooling on the rod became lighter in a few spots, but the change in color did not travel through the mass, as it does in pure potassium dichromate. A 5% sodium dichromate mixture on cooling turned lighter throughout, the color change traveling slowly. The resulting mass however adhered to the rod though it crumbled off easily when touched.

Cooling and ΔT curves were determined for the 5% and a 2.3% sodium dichromate mixture. The tube containing the 5% mixture cracked when the temperature reached 202° but the curves did not indicate the position of a transition point. The 2.3% mixture in one run cracked the tube at 215° and gave a slight but inconclusive break in the ΔT curve at 221° . A second run on the same mixture did not result in a cracked tube and gave no break in the ΔT curve.

Discussion

This binary system is of the simple eutectic type. That no extensive solid solution takes place is shown by the presence of a eutectic halt for mixtures far removed in composition from the eutectic mixture.

The results of efforts to measure a change in the transition point of potassium dichromate due to possible solid solution are inconclusive. Probably a slight amount of solid solution takes place which lowers the transition temperature and also slows the rate of transition.

That the transition point of pure potassium dichromate obtained in this work is higher than the values obtained by previous investigators is

(7) Mitscherlich, *Ann. Phys. Chem. Pogg.*, **28**, 120 (1833).

(8) "International Critical Tables," Vol. IV, p. 8.

(9) Robinson, Stephenson and Briscoe, *J. Chem. Soc.*, **127**, 547 (1925).

(10) Schemtschuschny, *Z. anorg. Chem.*, **57**, 267 (1908).

(11) Tammann, "Kristallisieren und Schmelzen," Leipzig, 1903, p. 262.

due probably to its detection by a differential temperature curve. It should be pointed out that one temperature used in standardizing the thermocouple was 231.9° (m. p. of Bureau of Standards tin) which is quite close to the temperature of the transition in question.

Résumé

The liquidus curve of the binary system potas-

sium dichromate–sodium dichromate has been determined. It is of a simple eutectic type.

The melting point of sodium dichromate and the transition point of potassium dichromate have been redetermined.

The effect of the presence of sodium dichromate on the transition point of potassium dichromate has been noted.

NEW YORK, N. Y.

RECEIVED JUNE 18, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ROCHESTER]

A Study of the Heat Capacity of Aqueous Solutions of Barium Chloride

BY CHESTER M. WHITE

Thomsen¹ measured the specific heat of barium chloride solutions at 18° while some years later Marignac² reported values at 24.5°. More recently Urban³ has determined the specific heat at several temperatures for a number of solutions. Also Tippetts and Newton⁴ have made e. m. f. measurements on barium amalgam cells at several temperatures from which differences in partial molal heat capacities may be calculated. By an indirect method Richards and Dole⁵ have probably obtained the most precise data for barium chloride solutions, although the precision of their experiments is somewhat in doubt. Specific heats were redetermined for these solutions to provide precise results by the direct method. They will be useful as a test of recent theories of strong electrolytes for higher valence salts. The measurements were made with a twin adiabatic calorimeter.⁶ While the general design of the apparatus was similar to that of Gucker,⁷ the precision was of the order of 0.02%. This paper will stress the changes which were made in the construction and operation of the calorimeter to increase the precision to 0.01%.

Experimental

Modified Apparatus.—Figure 1 shows the construction of one of the calorimetric units. A threaded joint was used to secure the calorimeters in place. Internally threaded

collars (A) and externally threaded rings (B) were cast of brass. These were sweated to the original annular rings (C) which were secured permanently to the studs on the calorimeter cover by four special nuts (D). Originally the calorimeters were sealed to the annular rings, but the ground joint was not water tight after being in use two years. A coating of litharge and glycerol was placed between the calorimeter cover and the ring so that the joint would be water tight. A coating of de Khotinsky cement (E) was placed around the outside of the joint as a further protection. The Dewar jars (F), which served as calorimeters, were sealed to the rings by litharge and glycerol.

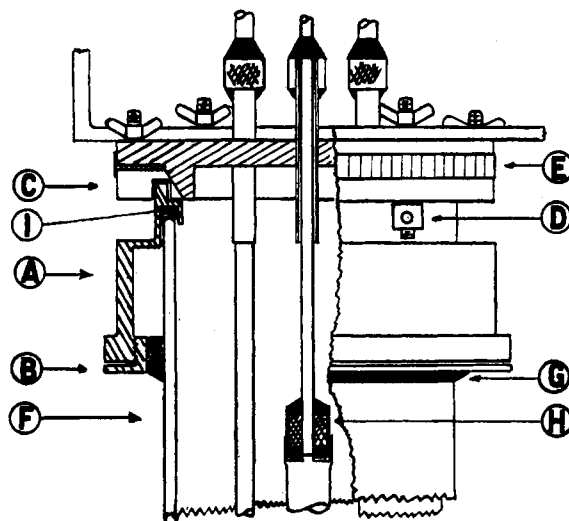


Fig. 1.—One unit of calorimeter.

After this mixture was dry, a 3.2-mm. coating of Bakelite cement (G) was applied above and below the litharge seal. After baking for a week at 60°, several coatings of Bakelite varnish were applied. The threads were lubricated with a water-proof grease, since the entire unit was submerged in water. The joint was entirely water tight during the entire series of measurements. A flat gasket (I) of soft rubber was fitted into the top of the collar so that the vapor

(1) Thomsen, "Thermochemische Untersuchungen," Leipzig, 1882.

(2) Marignac, "Oeuvres Complètes," Eggiman, Geneva, Vol. II, 1902, p. 624.

(3) Urban, *J. Phys. Chem.*, **36**, 1108 (1932).

(4) Tippetts and Newton, *THIS JOURNAL*, **66**, 1575 (1934).

(5) Richards and Dole, *ibid.*, **51**, 794 (1929).

(6) Unpublished work of Hess and Gramke; see B. E. Gramke, Master's Thesis, University of Rochester Library, 1930.

(7) Gucker, *THIS JOURNAL*, **50**, 1005 (1928).