[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF HAVERFORD COLLEGE AND THE UNIVERSITY OF NORTH CAROLINA]

The System Sodium Chromate–Sodium Molybdate–Water

BY WILLIAM E. CADBURY, JR.

In an earlier paper[1] the results of a study of the system sodium chromate–sodium sulfate–water were reported, with emphasis on the phenomena accompanying transition of decahydrate mixed crystals of the two salts into lower hydrates or anhydrous salt. Since sodium molybdate, like sodium chromate and sodium sulfate, is known to form a decahydrate, and since molybdates in general are analogous to sulfates and chromates, it was thought that a similar study of sodium chromate and sodium molybdate should prove interesting.

Two methods of approach were used: study of solubility relationships at various temperatures, and study of transition phenomena, similar to the study of the system sodium chromate–sodium sulfate–water mentioned above. The temperatures at which solubility studies were made were determined by the temperatures at which the various hydrates of these salts are known to be stable, and to a certain extent by information obtained and questions raised during the transition study. The solubility data were useful in interpreting the data on transition phenomena.

Information already available regarding the solid phases of these salts which can exist at ordinary temperatures may be summarized as follows[2,3]: Sodium chromate decahydrate is stable up to 19.525°, where it undergoes transition to sodium chromate hexahydrate, and it is metastable to 19.987°, where it undergoes transition to the tetrahydrate. The hexahydrate is stable from 19.525° to 25.90°, where it undergoes transition to the tetrahydrate. Below 25.90° the tetrahydrate is metastable with respect to the hexahydrate, but above 25.90° it is stable, until it in turn undergoes transition above 60° into the anhydrous salt. Sodium molybdate decahydrate is stable up to about 10°, where it undergoes transition to the dihydrate.

Experimental Part

Purification of Reagents.—C. P. grade sodium chromate and sodium molybdate were each recrystallized once as decahydrate and stored in a refrigerator. In the preparation of the desired mixtures, a second recrystallization was carried out, resulting in further purification.

Mixtures for Solubility Studies.—For the work at 0° and 8°, the desired amounts of the two salts were placed in a casserole and dissolved in a small amount of hot water. The solution was evaporated and chilled to obtain a supersaturated solution, which was then seeded with a crystal of decahydrate to produce decahydrate mixed crystals. These were separated from mother liquor by centrifuging, and placed in a large test-tube together with a little cold water. In some cases, the tube was then immersed in a constant temperature bath, so that equilibrium would be approached from undersaturation. In other cases, the mixture was warmed until the crystals underwent transition and largely dissolved. The mixture was then chilled and seeded again, before being placed in the bath, so that equilibrium was approached from oversaturation. The mixture was kept in the bath for several hours, with frequent stirring, in order to establish equilibrium. That equilibrium was reached in a few hours or less was shown by the fact that no significant difference in results was observed, either in the composition of the liquid or the solid, whether equilibrium was approached from undersaturation or oversaturation, or whether the mixture remained at the desired temperature for a few hours or for two weeks.

For the studies at higher temperatures, mixed crystals were prepared as described above and placed in a test-tube without additional water. The tube was then warmed to the desired temperature. If no transition took place, a little water was added. If transition did take place, a saturated solution was formed by the process of transition. In a few cases, where it was anticipated that the solid would be hexahydrate or tetrahydrate, the mixed crystals were dissolved by warming, then seeded at the proper temperature with hexahydrate or tetrahydrate. The mixture then was allowed to stand, with frequent stirring, for several hours at the desired temperature. Again, no difference was produced in the results by difference in technique.

Removal of Samples.—A few drops of the solution were withdrawn from the equilibrium mixture by suction through a sintered glass disk which was sealed to the end of a glass tube, and which had previously been brought to the same temperature as the mixture. The sample was then transferred to a weighing bottle. Except for the measurements at 8°, samples of the solid phase were separated from the mother liquor by centrifuging, using centrifuge cups which were as nearly as possible at the desired temperature. At 8°, the crystals were pressed between sheets of chilled filter paper to remove mother liquor. In either case, the slightly moist solids were then transferred to weighing bottles for analysis.

Analysis.—Water was determined from the loss in weight when the sample was heated to about 150° for five hours or more. Chromate was determined by titrating with ferrous ammonium sulfate, back-titrating with ceric sulfate, using ferroin as indicator. Recrystallized potassium dichromate was used as primary standard, and checks were made frequently against the recrystallized sodium chromate which was used in the actual investigation. Molybdate was determined by difference.

Transition Studies.—The technique was similar to that used in the study of sodium sulfate and sodium chromate.[1] Decahydrate mixed crystals, placed in a large test-tube, were warmed gently until partial transition took place. A calibrated thermometer was inserted, the tube was placed within a larger test-tube which acted as an air-bath, and the whole was immersed in a constant temperature bath at about the temperature of the mixture undergoing transition. The mixture was stirred frequently for an hour or more, after which the temperature of the mixture was read and a sample of the solution was removed through the glass disk mentioned above and transferred to weighing bottles for analysis.

Temperature Measurement.—Temperatures were measured with a thermometer, graduated in 0.1° intervals, which had been calibrated by the usual method against two thermometers previously standardized by the Bureau of Standards. The maximum deviation between the two calibrations was 0.03°, most of this deviation being attributable to uncertainty in the thermometer readings.

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[1] Cadbury, Meldrum and Lucasse, THIS JOURNAL, 63, 2262 (1941).

[2] Richards and Kelley, *ibid.*, 33, 847 (1911).

[3] Funk, *Ber.*, 33, 3696 (1900).

Results

Table I gives data on solubility measurements at the various temperatures. In order to save space, the data given are limited to a representative few of those obtained. Per cent. water is not given, but can be calculated by difference. The graphs as drawn include most of the points actually obtained, except where inclusion of several points close together would make the graphs appear cluttered. The form of each curve drawn is of course the same as on the original large-scale plot which contained every experimental point.

TABLE I

SYSTEM Na_2CrO_4–Na_2MoO_4–H_2O

Temp., °C.	Saturated solution		Moist solid		Solid phase
	% Na_2CrO_4	% Na_2MoO_4	% Na_2CrO_4	% Na_2MoO_4	
0	23.50	0	...	...	Decahydrate
	18.73	7.31	42.39	4.94	
	11.24	19.24	30.40	17.69	
	8.83	23.30	22.47	26.49	
	8.35	23.86	14.01	35.75	
	5.04	26.81	7.24	44.08	
	0	30.35	...	...	
8	30.50	0	...	...	Decahydrate
	25.49	7.16	41.49	4.64	
	22.44	11.56	38.12	7.92	
	19.36	16.45	35.12	12.06	
	13.07	25.35	23.76	23.64	
	20.59	19.64	23.91	23.09	
	15.22	24.27	15.55	31.37	
	9.44	29.25	10.94	37.44	
	3.21	33.97	3.63	47.18	
	0	36.83	...	...	
15	37.78	0	...	...	Decahydrate
	33.57	5.80	45.73	1.67	
	25.97	16.50	36.74	11.60	
	21.23	20.66	11.13	54.52	Dihydrate
	10.62	29.54	1.84	78.61	
	0	39.15	...	...	
19	43.09	0	...	...	Decahydrate
	40.85	3.20	45.65	2.37	
	38.55	6.45	44.21	4.30	
	43.82	0	...	...	Hexahydrate
	41.98	2.14	58.22	1.42	
	37.76	6.80	56.49	4.12	
	44.80	0.35	67.28	0.68	Tetrahydrate
	43.68	1.37	63.88	3.20	
	42.42	2.82	61.60	5.49	
	38.00	6.96	17.63	55.58	Dihydrate
	24.71	17.31	4.08	78.22	
	0	39.28	...	...	
22	44.98	0	...	...	Hexahydrate
	42.98	2.07	58.15	1.32	
	40.42	5.10	55.76	3.53	
	40.64	5.08	56.91	10.97	Tetrahydrate
	40.15	5.70	53.50	12.22	
	40.18	5.95	53.10	15.23	
25	45.85	0	...	...	Hexahydrate
	45.38	0.60	59.55	0.05	
	44.55	1.40	59.37	0.31	
	44.53	1.33	64.90	2.80	Tetrahydrate
	42.85	3.09	61.00	6.01	
	40.30	5.89	53.55	16.07	
	41.12	4.89	24.10	53.97	Dihydrate
	20.20	21.93	10.91	54.41	
	0	39.56	...	...	

Solubilities at 8°.—As a matter of convenience, the results obtained at 8° are discussed first. The data obtained at this temperature are plotted on rectangular coördinates in Fig. 1. The curve ACB represents the compositions of saturated solutions containing various proportions of the two salts. Individual points are represented by open circles, joined by tie-lines to the solid circles which represent the compositions of the moist solids in equilibrium with the various solutions. The actual composition of these solids, free from adhering solution, is given by the intersection of the tie-lines with the line EF, which represents the calculated compositions of mixed crystals containing ten moles of water per mole of total salt.

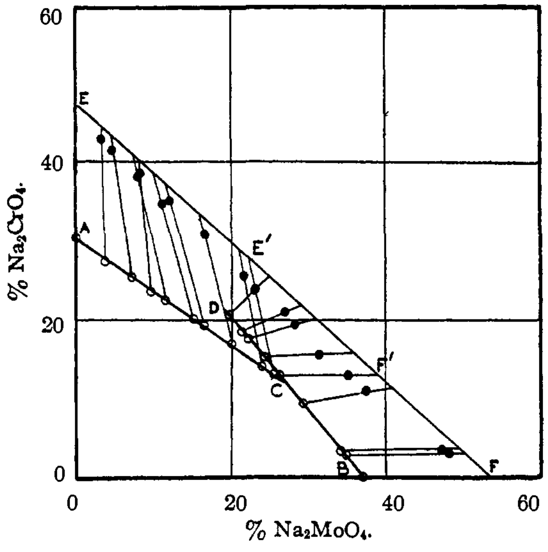

Fig. 1.—System Na_2CrO_4-Na_2MoO_4-H_2O at 8°.

The break, at C, in the curve ACB indicates a discontinuity in the solid solutions formed between the two decahydrates. Point C represents the composition of the isothermally invariant solution in equilibrium with the two solid solutions represented by points E′ and F′. Along the extension, CD, of the solubility curve BC, the solutions are in metastable equilibrium with solid solutions of composition beyond the limit of stability, F′. Although no similar metastable continuation of AC was observed, there is no reason to think that, given the proper conditions, it could not be observed.

What the conditions are which lead to the formation of metastable crystals is not completely clear, but certain observations of a general nature can be made which shed some light on this problem.

Both sodium chromate decahydrate and sodium molybdate decahydrate, as well as mixed crystals of the two salts in any proportions, are unstable at room temperatures. To obtain sodium chromate decahydrate in the first place, a cold supersaturated solution of sodium chromate was seeded with a crystal of sodium sulfate decahydrate, which is stable at room temperature and is readily available. Some of the sodium chromate decahydrate thus formed was then kept in a cold place for future seeding purposes. No change, other than the dissolving of the added salt, was observed when a supersaturated sodium molybdate solution was seeded with either sodium chromate or sodium sulfate decahydrate. If, however, a supersaturated solution of sodium chromate and sodium molybdate, containing not too high a proportion of sodium molybdate, was seeded with sodium chromate decahydrate, crystallization took place. A small portion of the crystals thus formed was used to seed a supersaturated solution containing a still higher proportion of sodium molybdate. Crystallization again resulted. These crystals were then used to seed pure sodium molybdate solution (or a mixture of sodium molybdate dihydrate and saturated solution of this salt), resulting in the formation of sodium molybdate decahydrate. This was of course slightly contaminated with the seeding crystal, but successive seeding of a series of sodium molybdate solutions soon resulted in the formation of sodium molybdate decahydrate free from chromate. Contrary to expectation, when sodium molybdate decahydrate was used to seed a supersaturated solution of sodium chromate, crystallization took place rapidly.

When a cold supersaturated solution very rich in chromate is seeded with decahydrate crystals of any composition, crystals rich in chromate are obtained. Crystals are obtained from a solution very rich in molybdate if it is seeded with crystals rich in molybdate, but no crystallization takes place if crystals rich in chromate are used for seeding. It is possible, to a certain extent at least, to control whether crystals rich in chromate or rich in molybdate are obtained from solutions containing approximately equal proportions of the two salts. A mixture, containing proportions of chromate and molybdate such that the composition of solution could fall along CD, generally gave a point along CD when seeded with crystals rich in molybdate, although in a few cases a spontaneous shift took place, giving a solution along AC, and crystals of composition between E and E′. In order for the molybdate-rich crystals to be obtained at all, a similar spontaneous change (although in the other direction) must have taken place at some point in the series of operations, described above, by which sodium molybdate decahydrate was originally obtained. That is, in one of the operations, crystals rich in molybdate must have been produced, even though the mixture was seeded with crystals rich in chromate.

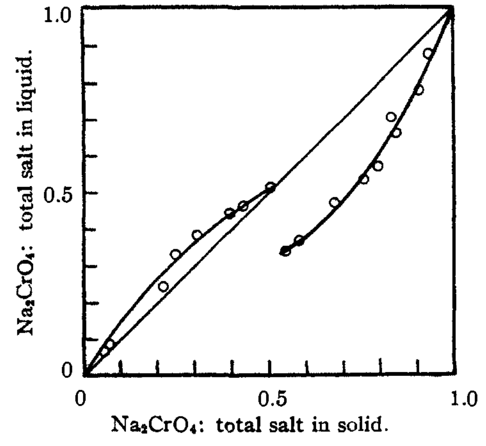

Fig. 2.—Distribution of sodium chromate between solid and liquid at 8°.

Although solid solutions of any composition desired can be prepared, it is evident that the crystals described here do not constitute a continuous series of solid solutions. This is emphasized by considering the distribution of the two salts in the solid and liquid phases. Let x be the ratio of sodium chromate to total anhydrous salt in the solid phase, and let y be the same ratio in the liquid phase. Plotting x against y, the diagram shown in Fig. 2 is obtained. It is evident from this diagram that there is a sharp discontinuity in the properties of the solid phase. The two curves lie on opposite sides of the 45° line. This system, therefore, falls into Roozeboom's[4] Type IV, which includes systems in which there is a discontinuity, and in which one salt is in greater proportion in the liquid than in one of the solids, while the same salt is in greater proportion in the other solid than in the liquid.[5]

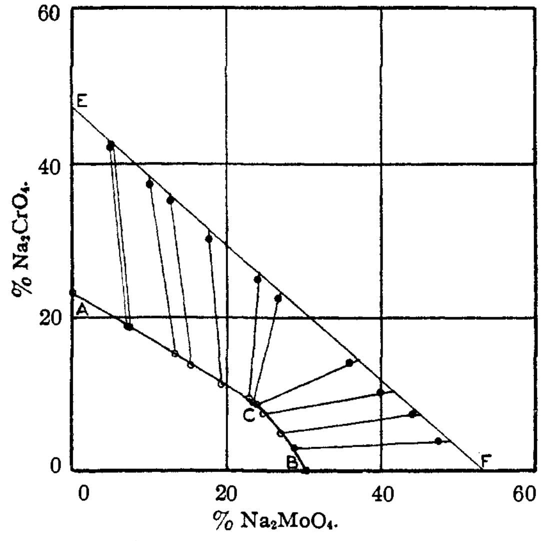

Fig. 3.—System Na_2CrO_4–Na_2MoO_4–H_2O at 0°.

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(4) Roozeboom, *Z. physik. Chem.*, **8**, 521 (1891).

(5) Blasdale, "Equilibria in Saturated Salt Solutions," The Chemical Catalog Co., Inc., New York, N. Y., 1927, p. 91.

Solubilities at 0°.—Figure 3 is a plot of the data obtained at 0°. The results are similar to those obtained at 8°, although the break in the curve is much less pronounced than at the higher temperature. The solid phase is in every case decahydrate mixed crystals. Crystals rich in chromate are in equilibrium with solutions represented by points along AC, and crystals rich in molybdate are in equilibrium with solutions along BC. No metastable equilibrium was observed at this temperature. That the discontinuity is less pronounced than at 8° is shown by Fig. 4, in which *x* is plotted against *y*, *x* and *y* having the same significance as before. In fact, from the data at hand, it cannot be said definitely that there is a discontinuity at this temperature.

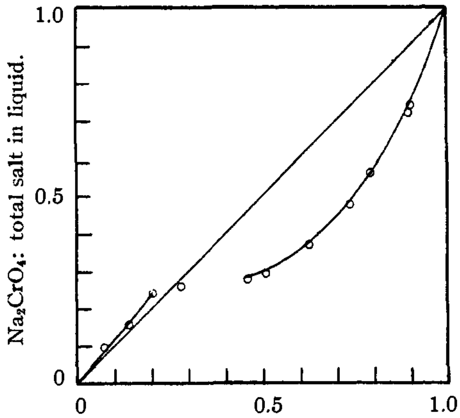

Fig. 4.—Distribution of sodium chromate between solid and liquid at 0°.

Solubilities at 15°.—Figure 5 is a plot of data obtained at 15°. The point A is the solubility of sodium chromate decahydrate at this temperature, and the curve AC represents the solubility of decahydrate mixed crystals of varying proportions of sodium chromate and sodium molybdate. That the crystals are relatively rich in chromate is shown by the slope of the tie-lines. The line EF represents the calculated compositions of decahydrate mixed crystals. The point B represents the solubility of sodium molybdate dihydrate, the form of sodium molybdate which is stable at this temperature. As the proportion of sodium chromate in the mixture increases, the solubility follows the curve BC. Since there is no break in this curve, the solid phase in equilibrium with solutions along this curve must be dihydrate.

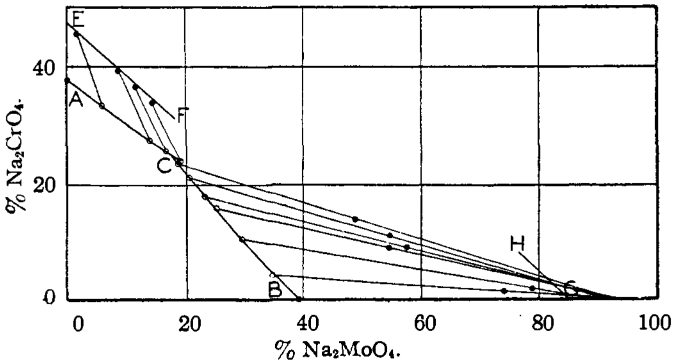

Fig. 5.—System Na_2CrO_4-Na_2MoO_4-H_2O at 15°.

The solid circles represent the compositions of moist crystals in equilibrium with the various solutions. The crystals in equilibrium with solutions between B and C are very fine, and retain much mother liquor even after prolonged centrifuging, so that direct analysis of the moist solid gives results far from the true composition of the solid phase, which, for dihydrate mixed crystals without adhering mother liquor, would lie along the line GH. It is evident that the tie-lines, extended, do not meet at point G, which represents pure sodium molybdate dihydrate, but spread out somewhat from that point, indicating mixed crystals of dihydrate containing a small amount of sodium chromate. (This spread is more clearly shown in Fig. 8, below.)

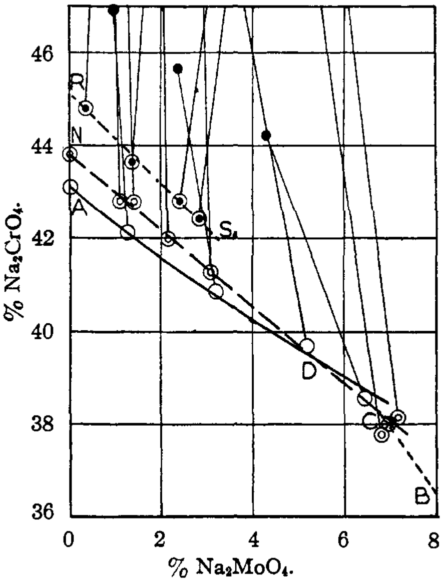

Fig. 6.—Part of system Na_2CrO_4-Na_2MoO_4-H_2O at 19°: ○, ——— decahydrate; ◉, — — — — tetrahydrate; ◎, — — hexahydrate; ⊗, - - - - - - dihydrate.

Solubilities at 19°.—Figure 6 is a plot of the solubility relationships at 19° when sodium chromate is in large excess. The curve CB is the start of the dihydrate curve: the rest of this curve is omitted, since it shows nothing new, being intermediate between Fig. 5 (15°) and Fig. 8 (25°).

The curve AD, perhaps extending beyond D into a metastable region, represents equilibrium between decahydrate mixed crystals and saturated solution. The curve NC represents equilibrium between hexahydrate mixed crystals and solution. The curves AD and NC are here drawn so that they cross at D, but since they are so nearly parallel it is not certain exactly at what point they cross, if at all. Assuming that they are drawn correctly, hexahydrate is metastable from N to D, then stable from D to C, at which point hexahydrate and dihydrate are in equilibrium with the same solution. The curve RS represents equilibrium between tetrahydrate mixed crystals and saturated solution. At all concentrations tetrahydrate is metastable (or unstable) at this temperature.

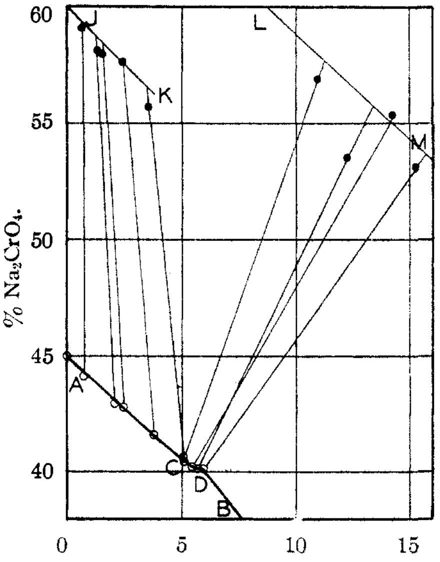

Fig. 7.—Part of system Na_2CrO_4–Na_2MoO_4–H_2O at 22°.

That the solid phase in equilibrium with solution along each of these curves is mixed crystals is shown by the fact that none of the sets of tie-lines converges at a point. The compositions of the mixed crystals are indicated by the slopes of the tie-lines. Decahydrate mixed crystals are relatively rich in chromate, hexahydrate mixed crystals contain a little more molybdate, and tetrahydrate mixed crystals contain more molybdate still.

Solubilities at 22°.—Solubility relationships at 22° when chromate is in large excess are illustrated in Fig. 7. Point A is the solubility of sodium chromate hexahydrate, the form of sodium chromate which is stable at this temperature, and the curve AC represents equilibrium between solutions and hexahydrate mixed crystals of sodium chromate and sodium molybdate, whose compositions, as calculated, are given by the line JK. At the point C, solution, hexahydrate mixed crystals, and tetrahydrate mixed crystals are in equilibrium. The short branch of the curve, CD, represents equilibrium between solution and tetrahydrate mixed crystals, whose compositions are calculated to lie along LM. The line DB shows the direction of the curve representing equilibrium between solution and dihydrate. The points C and D are of course invariant points at constant temperature and pressure.

The temperature of transition of sodium chromate hexahydrate to tetrahydrate is 25.90°.[2] From the fact that tetrahydrate becomes the stable phase, beyond point C, at this temperature, we see that sodium molybdate, present in the proportions indicated by the location of point C, lowers the temperature of this transition to 22°.

The distribution of the two salts between liquid and solid phases is brought out clearly by the slopes of the tie-lines. Calculation shows that, in the case of the hexahydrate mixed crystals, the ratio of sodium chromate to dried salt is greater in the solid than in the liquid phase, whereas in the case of the tetrahydrate the ratio of sodium chromate to dried salt is greater in the liquid than in the solid phase. A similar conclusion can be reached from the data at 19°.

Solubilities at 25°.—Figure 8 is a plot of data obtained at 25°. The curve BD is, as before, the solubility curve for dihydrate mixed crystals rich in molybdate. At D, solution, dihydrate, and tetrahydrate mixed crystals exist in equilibrium. Along DA the solid phase is tetrahydrate, until very near to the point A, which represents the solubility of sodium chromate hexahydrate. DA is really two curves. The first, the tetrahydrate curve, extends from D to a point near A, where a break in the curve would show the appearance of a new solid phase, the hexahydrate. From this point to A would then be the hexahydrate curve. The temperature, 25°, is so near to 25.90°, the temperature of transition of sodium chromate hexahydrate into the tetrahydrate, that very little molybdate is needed to lower the transition temperature to 25°. Therefore the hexahydrate curve is very short, and the expected break in the curve fails to show clearly. The lines GH, JK and LM represent again the cal-

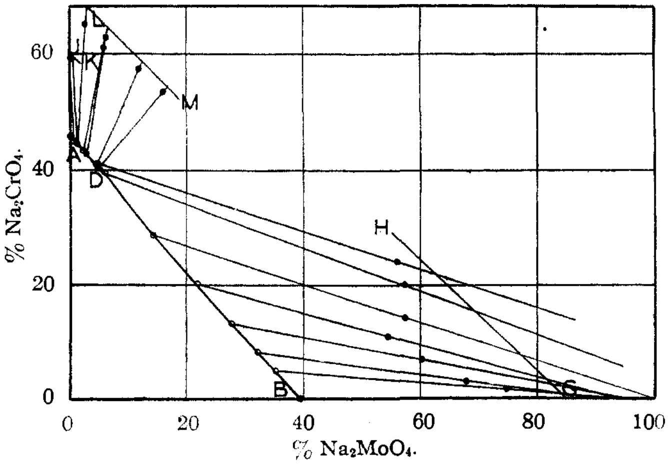

Fig. 8.—System Na_2CrO_4–Na_2MoO_4–H_2O at 25°.

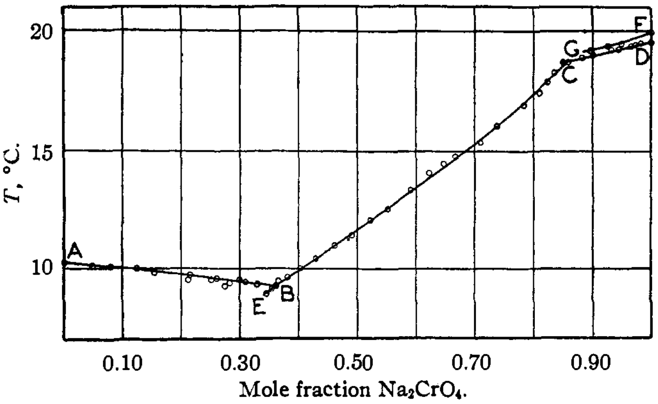

Fig. 9.—Temperatures at which liquids of various compositions are in equilibrium with two or more solids.

culated compositions of dihydrate, hexahydrate, and tetrahydrate mixed crystals, respectively.

Transition Phenomena.—The data in the present paper on the solubility of sodium molybdate, as well as the data of Funk,[3] indicate a temperature of transition from decahydrate to dihydrate somewhat above 10°. The equilibrium method, the same as that used by Richards in his classical determination of the transition temperatures of sodium sulfate[6] and sodium chromate,[2] gives for sodium molybdate 10.27°. Although this result is less reproducible than the result for either sodium sulfate or sodium chromate, it is much more precise than can be obtained by the solubility method. The uncertainty, caused by lack of reproducibility, possible error in calibration, and error in reading the thermometer, is probably less than ±0.05°.

Although the transition temperature of a hydrated salt is an invariant point at constant pressure, the temperature at which hydrated mixed crystals undergo transition depends upon the composition of the system. If the solution formed by transition has a definite composition, the temperature at which two solid phases can exist in equilibrium with that solution is fixed; but if the composition changes, then the temperature will change also, provided that all three phases remain.[7]

In Fig. 9 the temperatures at which saturated solutions are in equilibrium with two or more solids are plotted against composition of solution, expressed as mole fraction of sodium chromate in total dried salt, *i. e.*, moles of sodium chromate divided by moles of sodium chromate plus moles of sodium molybdate. The data are not tabulated, since they can be read with sufficient precision from the graph.

Points A and D are, respectively, the transition temperatures of sodium molybdate decahydrate to dihydrate and sodium chromate decahydrate to hexahydrate. Each line on the diagram represents temperatures at which saturated solutions of the compositions indicated are in equilibrium with two solids. Along AB the solids are dihydrate mixed crystals, containing very little sodium chromate, and decahydrate mixed crystals, rich in molybdate. Along CB (and its continuation, BE) the solids are dihydrate mixed crystals, as before, and decahydrate mixed crystals, rich in chromate. Along CD the solids are decahydrate and hexahydrate mixed crystals, both rich in chromate.

Point F represents the metastable transition temperature of sodium chromate decahydrate into the tetrahydrate. This metastable point, as has been pointed out before,[1,2] can be realized experimentally, by warming decahydrate crystals rapidly, but only if no hexahydrate whatever is present, even as dust in the atmosphere. By making measurements in midsummer, when all traces of hexahydrate had been destroyed by the heat, it was possible to obtain experimentally this point and three points along the curve FG. Along this curve saturated solutions are in metastable equilibrium with decahydrate and tetrahydrate mixed crystals.

The points B and C are invariant points at constant pressure, at which four condensed phases are in equilibrium. At B these phases are solution, dihydrate mixed crystals, and decahydrate mixed crystals in two phases: one rich in chromate, the other rich in molybdate. At C the four phases are solution, dihydrate, hexahydrate, and chromate-rich decahydrate mixed crystals.

The diagram, Fig. 9, is actually a projection against the sodium chromate–sodium molybdate face, according to the Jänecke method,[8] of the three-dimensional prism diagram representing the polytherm of the system sodium chromate–sodium molybdate–water. Figure 9 includes only those equilibria which involve saturated solutions and decahydrate mixed crystals as two of the phases. Other equilibria are possible, for some of which a few data are already at hand from the isothermal solubility studies. One such curve extends downward from B, representing equilibrium between saturated solutions and the two limiting decahydrate solid solutions. At B these limiting solid solutions are in equilibrium, at 9.25°, with a liquid solution containing 0.362 mole fraction of sodium chromate in the dried salt from solution. At 8°, point C, Fig. 1, gives 0.349 mole fraction for the composition of the saturated solution in equilibrium with these two solids, and at 0°, point C, Fig. 3, gives 0.316 mole fraction sodium chromate (provided there actually is a discontinuity in the isothermal solubility curve at 0°). If this discontinuity persists to still lower

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(6) Richards and Wells, *Proc. Am. Acad. Arts Sci.*, **38**, 43 (1902); *Z. physik. Chem.*, **43**, 465 (1903).

(7) For a more detailed discussion, see ref. 1, p. 2266.

(8) For an example, see Blasdale, *loc. cit.*, p. 79.

temperatures, the curve may reach to a ternary eutectic involving ice and the two solid solutions in equilibrium with saturated liquid solution.

Comparison between results from the solubility studies and from the transition studies gives fairly good agreement. At 15° (point C, Fig. 5) decahydrate, dihydrate and solution are in equilibrium at a composition, mole fraction sodium chromate in dried salt from solution, 0.64, compared with 0.68 from the transition data, Fig. 9. At 19° decahydrate, hexahydrate and solution are in equilibrium at a composition 0.90 (point D, Fig. 6) compared with 0.90 from Fig. 9. (In view of the uncertainty in the location of point D, Fig. 6, this agreement is somewhat fortuitous.)

Summary

1. Solubility equilibrium relationships in the system sodium chromate–sodium molybdate–water have been investigated at 0, 8, 15, 19, 22 and 25°.
2. A discontinuity probably appears at 0°, and definitely appears at 8°, in the series of solid solutions formed by the decahydrates of the two salts. In addition to the stable solid solutions, metastable decahydrate solid solutions rich in sodium molybdate were prepared at 8°.
3. Sodium molybdate dihydrate takes up only a small amount of sodium chromate in solid solution.
4. Sodium chromate hexahydrate takes up some sodium molybdate in solid solution, and sodium chromate tetrahydrate takes up still more, at temperatures where these hydrates can exist, either as stable or as metastable phases.
5. The temperature of transition of sodium molybdate decahydrate into the dihydrate is 10.27 ± 0.05°.
6. The relationship was investigated between composition of solution and the temperature at which decahydrate solid solutions can exist in equilibrium with liquid solutions and another solid phase.
7. Decahydrate solid solutions rich in molybdate always undergo transition to dihydrate when warmed. Decahydrate solid solutions rich in chromate likewise change to dihydrate, except when chromate is in great excess, in which case the change is to hexahydrate, or, under special conditions, to tetrahydrate.

HAVERFORD, PA. RECEIVED OCTOBER 23, 1944

[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1a]]

A Tensiometric Method for Evaluating Surface Wettability by Measurement of the Contact Angle

BY HELMUT WAKEHAM AND EVALD L. SKAU

The surface wettability of a solid by a liquid such as water is generally evaluated in terms of the work of adhesion between the solid and the liquid as defined by the equation $W = \gamma (1 + \cos \theta)$ where γ is the liquid to air surface tension and θ is the angle of contact between the solid and liquid.[1b] For a given value of the surface tension, γ, the work of adhesion is a function of the contact angle, θ; thus for small values of θ, W is large and the solid is more readily wet by the liquid than when θ is large.

The paper and textile industries have recognized the importance of the contact angle in the evaluation of wettability.[2–8] The method of measurement in most applications, however, requires the use of specialized and expensive optical equipment and is not conducive to rapid routine measurement. The present paper outlines the basis for a simple contact angle measurement by means of a Cenco-du Nouy interfacial tensiometer and illustrates the application of the method to several different types of samples which might be encountered when the wettability of the substance is to be measured.

In this method the sample in the form of a circular disk one-half inch in diameter is adjusted to a position parallel to the surface of the water and then pressed with gradually increasing force down into the surface (Figs. 1 and 2). As the disk is pushed down the angle which the edge of the water makes with the upper surface of the sample gradually increases. The maximum value which this angle can attain is the advancing contact angle; when the sample is pushed further down the hydrostatic pressure of the water at the edge of the sample causes the water to move across the surface of the sample. The contact angle is, thus, a function of the force or the maximum reading on the tensiometer measured at the moment that the liquid surface breaks and the sample submerges.[9]

(1) (a) This is one of four regional research laboratories operated by the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(1) (b) N. K. Adam, "The Physics and Chemistry of Surfaces," Oxford University Press, New York, N. Y., 3rd ed., 1941, p. 179.

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(9) The relation between force applied in dynes, and tensiometer reading will be the same for different interfacial tensiometers when the instruments are calibrated according to the manufacturer's directions for rings of 6.00-cm. mean circumference.