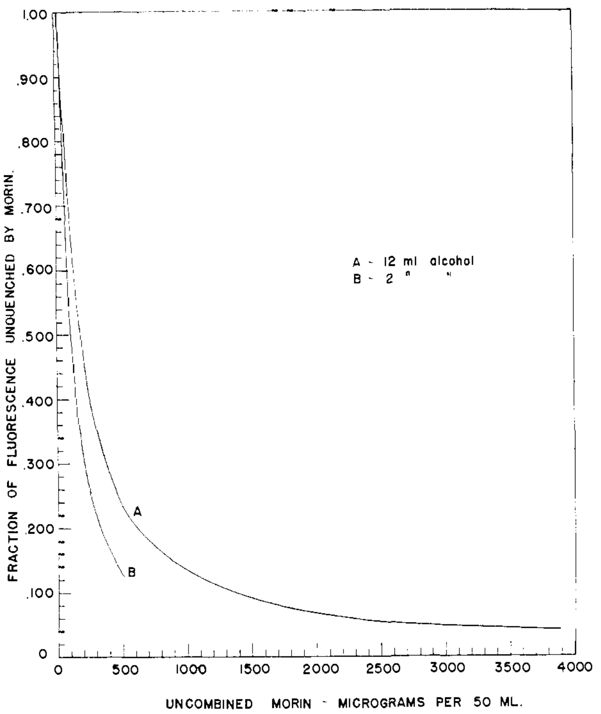

Fig. 12.—Fraction of fluorescence remaining unquenched as a function of the uncombined morin. Thorium constant at 50.3 μg. of ThO_2 per 50 ml. Curve A, 12 ml. of alcohol; curve B, 2 ml. of alcohol; P_0 (404.7 mμ).

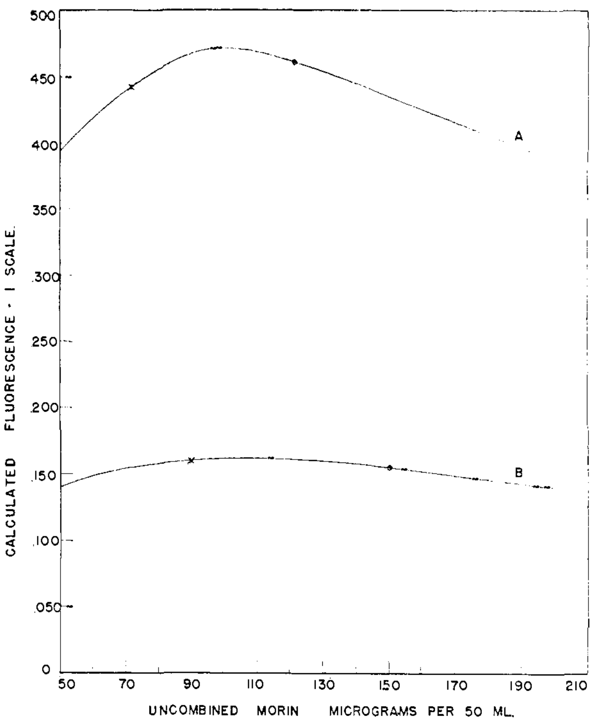

Fig. 13.—Calculated fluorescence as a function of uncombined morin in the solutions: curve A, total thorium 50.3 μg. of ThO_2 per 50 ml.; curve B, total thorium 15 μg. of ThO_2 per 50 ml.; 2 ml. of alcohol; P_0 (404.7 mμ).

15 μg. of ThO_2. *CR* was evaluated using the mass action law

$$\frac{(CR)(\mathrm{H}^+)^2}{(\mathrm{ThO_2} - CR)(\mathrm{M\cdot H} - 2CR)^2} = K_\mathrm{E}$$

where

(CR) = complex formed, moles per liter
$(\mathrm{M\cdot H})$ = total morin, moles per liter
$(\mathrm{M\cdot H} - 2CR)$ = uncombined morin, moles per liter
$(\mathrm{ThO_2})$ = total thorium, moles per liter
$(\mathrm{ThO_2} - CR)$ = uncombined thorium, moles per liter
K_E = equilibrium constant

K_E had been determined previously[5]; for thorium concentrations in the range of the standard curve the average values of K_E are 1.45×10^6 when total morin is 100 μg., and 0.95×10^6 when total morin is 165 μg.

The calculated standard curves are shown in Figs. 6 and 7 as dashed lines; they coincide very closely with the experimental curves. Both the region of linearity and slope predicted by the calculated curves are corroborated by the experimental curves. It is possible, thus, to use the derived mathematical expressions for fluorescence to calculate a family of curves that show, without actual experimentation, the characteristics of the standard curves to be expected for total morin concentrations that vary over a wide range.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF ARKANSAS]

Color Transitions in Fused Nickel(II)–Alkali Halide Systems

BY FREDERICK M. HORNYAK[1]

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Nickel(II) chloride (or sulfate) fused with alkali chlorides or bromides gives, respectively, a blue or green melt. On cooling a yellow solid is formed. The color transition is abrupt and reversible and occurs very close to the melting point.

During the course of work on molten salt systems it was observed that fusion of yellow anhydrous nickel(II) chloride and potassium chloride gives a blue liquid. On cooling, the melt becomes a blue semi-solid and finally over a short temperature interval undergoes a striking color transition to a yellow solid. Since materials which undergo distinct color changes at definite temperatures are rather rare it was decided to observe various fused salt systems to determine the generality of the phenomenon. The relationship of color transition temperatures to phase transition temperatures was also investigated.

Observations and Discussion.—The nickel chloride–potassium chloride system exhibited the phenomenon for all compositions having a nickel

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chloride mole fraction of 0.4 or less. Mole fractions above 0.4 were difficult to work with and were not investigated. The color appears to be quite intense; 10 mg. of nickel chloride imparts a pale blue color to 10 g. of potassium chloride melt. The color transition is reversible and may be repeated indefinitely except for slight nickel chloride decomposition at the melt surface in the presence of oxygen.

About 5% by weight of $NiCl_2$ was fused with alkali chlorides from lithium through rubidium, respectively, and the abrupt blue-yellow color transition was found to occur in each case.

Cesium chloride behaved anomalously. The melt was deep blue but on cooling to the solid state blue spots were sometimes left in a yellowish matrix and at other times a uniform pastel blue resulted. The melt was stirred before cooling and the cause of the variable behavior remains unknown. The blue color was quickly discharged on standing in moist air but was stable when the solid was stored in a desiccator. It is worthy of note that CsCl also distinguishes itself from the other alkali chlorides in having a different crystal lattice type.

Fusion of nickel chloride with sodium or potassium bromide gave an abrupt reversible transition from green to yellow on cooling. Alkali iodides were too unstable to observe. A nickel chloride–sodium fluoride melt produced a light green solid with no definite visual changes.

The same reversible blue-yellow and green-yellow transitions were observed when nickel(II) sulfate was fused with sodium or potassium chlorides or bromides, respectively. Fusion of $NiCl_2$ with potassium or sodium sulfate or with the chlorides of Hg(II), Pb(II), Ca(II) or Cd(II), respectively, produced brown melts which gradually yellowed on cooling.

No distinct color transitions were observed when KCl was fused with the chlorides of Cd(II), Mn(II), Pd(II), Co(II) or Pb(II), respectively. Fusion of cobaltous chloride with KCl produced dark blue solutions which on solidification remained a lighter blue, the color of anhydrous $CoCl_2$. Senderoff and Brenner[2] observed that the fusion of yellow $MoCl_2$ with a eutectic LiCl–KCl mixture produced a bright red mass which they considered indicative of complex halide formation. The color did not discharge on cooling as in the case of nickel.

These observations, although not exhaustive, indicate that the color transition is uniquely characteristic of Ni(II) ion in the presence of sufficient amounts of chloride or bromide ion. The alkali chlorides or bromides appear to be particularly favorable to the effect.

Melting Point Studies and Discussion.—Cooling curves for various KCl–$NiCl_2$ compositions were run using a thermocouple and potentiometer and a partial phase diagram was constructed (Table I). A eutectic point was found at 508° and a potassium chloride mole fraction of 0.75.

By visual observation the temperature of color transition for the various mixtures was found to be 503 ± 4° which is close to the eutectic temperature.

TABLE I

FREEZING POINT *vs.* COMPOSITION FOR THE SYSTEM KCl–$NiCl_2$

Mole fraction KCl	F.p. (°C.)	Mole fraction KCl	F.p. (°C.)
1.00	774	0.78	560
0.93	735	.75	508
.85	675	.70	575
.80	600	.60	625

Visual observations and cooling curves for other alkali halide–$NiCl_2$ mixtures gave results as shown in Table II.

TABLE II

COLOR TRANSITION *vs.* MELTING POINT (°C.)

Mixt.	Parts by wt.	M.p., °C.	Color trans. (±8°)
1	$3NiCl_2$–7NaCl	568	566
1a	$0.01NiCl_2$–1NaCl		549
2	$1NiCl_2$–1LiCl–1KCl	366	354
2a	$0.01NiCl_2$–1LiCl–1KCl		351
3	$1NiCl_2$–3KBr	457	449
4	$1NiCl_2$–1KBr–1NaBr	477	471

Melting points were determined as the final slope change on the cooling curves; mixtures 1 and 2 showed constant temperature plateaus whereas 3 and 4 gave less definite breaks suggesting solid solution formation.

These data strongly indicate that color transitions take place at the melting point. The color is due apparently to a Ni(II)–halide interaction such as solvation or complex ion formation which is made possible by the formation of the liquid state. Evidence for the association of halide with other cations in fused alkali chlorides has been given by Senderoff and Brenner.[2] No such colored Ni(II)–halide association has been found in aqueous solution where of course the halide density is much less.

The change in melt color from blue to green on changing the halide environment from chloride to bromide is in harmony with the concept of "color deepening"[3] which results from a bathochromic shift of absorption band due to the increasing mass of the associating anions.

Experimental

For a cooling curve determination the salt mixture weighing about 15 g. was placed in a porcelain crucible at the bottom of a well-type insulated electric furnace. A Leeds and Northrup Co. type K-2 potentiometer was used with a chromel–alumel thermocouple immersed in the center of the salt mixture. The furnace well was covered with an asbestos lid and flushed with nitrogen *via* a Vycor tube. After liquefaction the melt was stirred with the thermocouple and cooling curve data taken in the usual way. Corrections were made for a room temperature reference junction. The error in melting points is estimated to be ±3°. The uncertainty of ±4–8° in the visually observed color transition temperature was due to some difficulty in balancing the potentiometer at the proper time. The color change began at the cooler, outermost parts of the melt first and then proceeded toward the center.

Analytical reagents were used. Anhydrous $NiCl_2$ was

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(2) S. Senderoff and A. Brenner, *J. Electrochem. Soc.*, **101**, 30 (1954).

(3) W. R. Brode, *Am. Scientist*, **43**, 259 (1955).

prepared from the hydrate by pulverizing and heating. The salt mixtures were made up by weight and the nickel content of several melts was checked by the dimethylglyoxime method. Decomposition to water insoluble compounds was always less than 1%.

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[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS EXPERIMENT STATION, REGION II, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Low Temperature Heat Capacities and Entropies at 298.15°K. of Some Crystalline Silicates Containing Calcium

BY E. G. KING

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Heat capacity measurements from 51 to 298°K. were conducted for γ-calcium orthosilicate, tricalcium disilicate, diopside (calcium–magnesium metasilicate) and anorthite (calcium–aluminum silicate). The entropies at 298.15°K. are, respectively, 28.8 ± 0.2, 50.4 ± 0.3, 34.2 ± 0.2, and 48.4 ± 0.4 cal./deg. mole. Entropies of formation of the silicates from their constituent oxides are derived.

Low temperature heat capacity and entropy data are available for two varieties of calcium metasilicate[1–4] ($CaSiO_3$, wollastonite and pseudowollastonite), one variety of calcium orthosilicate[5] ($Ca_2SiO_4(\beta)$, thermodynamically unstable form), and tricalcium silicate[5] (Ca_3SiO_5). This paper reports low temperature heat capacity data and entropy evaluations at 298.15°K. for four additional crystalline silicates containing calcium, (1) the room temperature stable form of calcium orthosilicate ($Ca_2SiO_4(\gamma)$), (2) tricalcium disilicate ($Ca_3Si_2O_7$), (3) diopside ($CaMgSi_2O_6$), and (4) anorthite ($CaAl_2Si_2O_8$). No previous similar data exist for these substances, except some heat capacity values for diopside between 20 and 40°K. (reported by Wagner[2]) which are insufficient for evaluation of the entropy at 298.15°K.

Materials.—The γ-calcium orthosilicate was part of the sample described by Coughlin and O'Brien.[6] It contained 34.88% silica (theory, 34.89%) and gave an X-ray diffraction pattern that agreed with the ASTM catalog.

Tricalcium disilicate was made by heating a stoichiometric mixture of reagent-grade calcium carbonate and pure silica for a total of 80 hours at 1100–1200° and 12 hours at 1200°, with intervening grindings, mixings, analyses and adjustments of composition.[7] The final product contained 58.37% lime and 41.62% silica, as compared with the theoretical 58.33 and 41.67%. The X-ray diffraction pattern checked the ASTM catalog.

The diopside was natural mineral from Juva, Finland. It was supplied by Prof. Th. G. Sahama of the University of Helsinki, who also furnished the chemical analysis. As received, it contained 0.22% water which was removed by heating to 700° before use. It contained (on a dry basis) 25.91% lime, 18.82% magnesia, 54.78% silica, 0.68% ferric oxide, 0.07% ferrous oxide, 0.07% alumina, 0.02% manganous oxide and no titania. (The theoretical analysis for pure diopside is 25.89% lime, 18.62% magnesia and 55.49% silica.) The optical properties and density checked closely the accepted values for diopside. Further details regarding this sample are given by Juurinen and Hytonen.[8]

Anorthite was prepared by repeated sintering of a stoichiometric mixture of reagent-grade calcium carbonate, pure hydrated alumina and pure silica, with the usual intervening grinding, mixing, analysis and adjustment of composition.[9] Nine heats were made, totaling 58 hours at 1100°, 53 hours at 1200°, 6 hours at 1300°, and 10 hours at 1500°. A platinum container was used for the 1500° heats and Alundum for the others. The product analyzed 20.10% lime, 36.64% alumina, 43.02% silica and 0.20% ferric oxide. (The theoretical analysis is 20.16% lime, 36.65% alumina and 43.20% silica.) The X-ray diffraction pattern checked that given in the ASTM catalog for synthetic anorthite.

Heat-Capacity Measurements and Results.—The measurements were conducted in previously described apparatus.[10] The sample masses were as follows: γ-calcium orthosilicate, 116.94 g.; tricalcium disilicate, 114.75 g.; diopside, 209.83 g.; and anorthite, 184.02 g. All weighings were corrected to vacuum and all molecular weights conform with the 1954–55 Report on Atomic Weights.[11] The definition 0°C. = 273.15°K. was employed. The precision uncertainty in the heat capacity measurements is less than 0.1% and the absolute error is considered to be 0.3%.

The heat capacity results, expressed in defined calories (1 cal. = 4.1840 abs. joules) per deg. mole, are listed in Table I. The four substances exhibit normal heat capacity curves over the entire temperature range investigated.

At room temperature the heat capacities of these silicates do not differ greatly from the sums for their constituent oxides. The difference is smallest for anorthite (0.2%) and greatest for γ-calcium orthosilicate (2.5%). It is of interest to note that the heat capacity of the γ-variety of calcium orthosilicate is lower than that of the β-variety[5] by amounts ranging from 1.4% at 298°K. to 12.4% at 50°K.; this is to be expected as the β-variety is thermodynamically unstable. Diopside may be considered as composed of one mole each of calcium metasilicate and magnesium metasilicate. In comparison with wollastonite and clinoenstatite[4] its heat capacity is lower by 0.5% at 298°K. and 23.8% at 50°K. Anorthite may be compared with its so-

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[2] H. Wagner, *Z. anorg. Chem.*, **208**, 1 (1932).

[3] S. Cristescu and F. Simon, *Z. physik. Chem.*, **25B**, 273 (1934).

[4] K. K. Kelley, U. S. Bur. Mines Bull. 477 (1950).

[5] S. S. Todd, THIS JOURNAL, **73**, 3277 (1951).

[6] J. P. Coughlin and C. J. O'Brien, *J. Phys. Chem.*, **61**, 767 (1957).

[7] This substance was prepared by K. R. Bonnickson, formerly Chemist, Minerals Thermodynamics Experiment Station, Reg. II, Bureau of Mines.

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