rise at the transition temperature which indicates an increase in ionic conductivity at that point. However, the slope of the β-phase curve is lower than that of the α. Since this indicates a lower Q for the β-phase than for the α-phase, the data do not fit directly into the Ketelaar scheme. It may be that the lower Q is due to the presence of electronic conductivity which would contribute a higher percentage of the current to the β-phase than to the α. A knowledge of the percentage electronic conductivity would be required to solve for Ketelaar's V. Electronic current carriers might be expected to be of less importance in the eutectoid
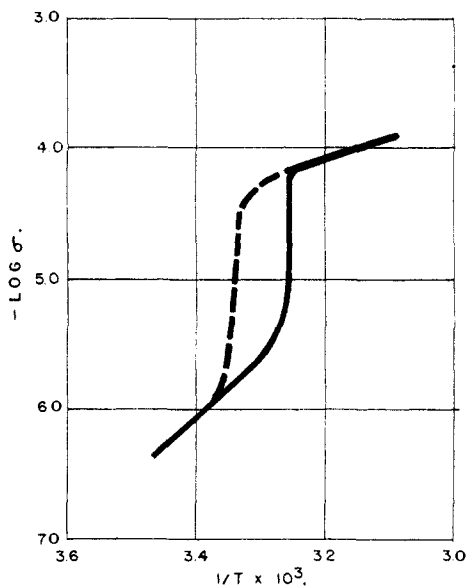

Fig. 2.—Hysteresis loop found for eutectoid: ---, increasing temperature; — — — —, decreasing temperature.

with its highly mobile silver ions and, therefore, the β-phase Q is again higher than that for the α-phase. The values found for Q and σ_0 in all preparations are given in Table III. The Q-values for the eutectoid are not averages, but are instead outside the ranges bounded by the values for the parent compounds (resulting in a minimum for α and a maximum for β).

TABLE III
CONDUCTIVITY DATA

Substance	σ_0 (ohm $^{-1}$ cm. $^{-1}$)	Q (kcal./g. atom)
β-Ag$_2$HgI$_4$	1.4×10^6	16.4
α-Ag$_2$HgI$_4$	7.5×10^3	10.2
β-Cu$_2$HgI$_4$	2.2×10^{-1}	8.9
α-Cu$_2$HgI$_4$	3.3×10^3	13.7
β-Ag$_{1.14}$Cu$_{0.86}$HgI$_4$	4.2×10^{19}	19.7
α-Ag$_{1.14}$Cu$_{0.86}$HgI$_4$	9.1	7.4

The compounds and the eutectoid exhibit a temperature lag in the transition point on cooling. Figure 2 is a plot of the data obtained in a typical run with the eutectoid in which conductivity values were obtained both upon increasing and decreasing the temperature. The result is a hysteresis loop which indicates a temperature lag of about 8° on cooling. This checks observations of the color change in the free powder, but is considerably less than the lag previously reported[3] where the powder was bound in a silicone lacquer and observed for color change. It therefore appears that the lacquer serves to insulate grains against each other and thus minimize spread of nuclei. The more gradual change in conductivity on cooling as compared with the sharp change on heating corresponds to the visual observations in the previous paper.[3]

FORT MONMOUTH, N. J.

Calorimetric Determination of the Freezing Point of Phthalic Anhydride

BY A. C. WERNER AND S. V. R. MASTRANGELO[1]

The triple point of pure phthalic anhydride, determined in an adiabatic calorimeter, was 131.10°. Sources of error in previous determinations are analyzed. The effect of pressure on the melting temperature, independent of the effect of dissolved air, was 0.033° per atmosphere. The difference between the freezing point and the triple point was 0.012°. The effect of phthalic acid, benzoic acid, maleic acid, fumaric acid, maleic anhydride, 1,4-naphthoquinone and phthalimide, singly, in pairs and altogether, on the freezing point of phthalic anhydride has been determined for the first time. Normal behavior was encountered on all systems but the pair benzoic acid and phthalic acid. When this pair is present, deviation from ideal behavior occurs due to solid solution formation.

Introduction

Several values have been reported for the freezing point of pure phthalic anhydride. Monroe[2] has reported 130.84°; Debeau,[3] 130.95°; and Burriel-Marti,[4] 131.60°.

Monroe's method did not permit calculation of the freezing point of 100 mole per cent. material. Debeau employed the method of Glasgow, Streiff

and Rossini,[5] which usually permits such a calculation to be made. However, we have found that this method does not give consistent values of the freezing point of pure phthalic anhydride, presumably because its crystallization rate is such that equilibrium is not maintained at all times. It was necessary, therefore, to determine first the triple point of pure phthalic anhydride by data obtained in an adiabatic calorimeter on a specially purified sample, and then to add to this figure the difference

(1) To whom inquiries may be directed.
(2) K. P. Monroe, *Ind. Eng. Chem.*, **11**, 1116 (1919).
(3) D. E. Debeau, THIS JOURNAL, **68**, 2725 (1946).
(4) F. Burriel-Marti, *Bull. soc. chim.*, **39**, 590 (1930).

(5) A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

between the freezing point and the triple point obtained by observing time–temperature relationships with very small cooling rates.

Experimental

Materials.—The phthalic anhydride used in the calorimetric determinations was prepared from Barrett phthalic anhydride by recrystallization twice from the melt, followed by $1^1/_4$ hours of refluxing and simple distillation. This material was 99.95 mole per cent. pure. The sample used for determination of the difference between freezing and triple point was prepared by refluxing and simple distillation. Commercial Barrett phthalic anhydride was used for the freezing point depression and dilatometric measurements. With the exception of phthalic acid, which was prepared by hydrolysis of phthalic anhydride and recrystallization twice from water, the remaining materials were the best commercial grades available and were used without further purification.

Freezing Points.—The apparatus was constructed according to Glasgow, Streiff and Rossini.[5] However, because of lack of equilibrium between the crystalline and liquid phases, their method of extrapolating the time–temperature freezing curves to obtain freezing points could not be used with these systems. Hence, the freezing point was taken as the highest temperature reached after crystallization had started. Cooling rates of 0.25–0.5° per minute were used in these measurements. The validity of the procedure was demonstrated by the good agreement observed between the freezing point depression obtained in this way and in the triple point calorimeter.

Calorimeter.—The calorimeter sample vessel is shown in Fig. 1. The design is based on those of Lange[6] and Southard and Brickwedde.[7] The calorimeter sample vessel was constructed of nickel. Welded seams were used wherever liquid or solid material came in contact with the calorimeter. Other permanent joints were made of silver solder. Soft solder was used only at the final sealing points, 9 and 11. A more detailed description of the calorimeter is offered by the legend which accompanies Fig. 1.

The calorimeter assembly of Southard and Brickwedde[7] was modified for high temperature work. Sauereisen cement was used to secure the heating elements to the shields and to provide thermal contact between the thermometer-heater and the sample vessel temperature equilibration ring, 3.

A special Leeds and Northrup platinum thimble type calorimetric platinum resistance thermometer, 1, modified for use at high temperature, was used as a combination heater and thermometer. This thermometer was filled with dry air at 0.5 atmosphere pressure. A special glass with low conductivity at high temperatures was used for the cap. The thermometer was calibrated by the National Bureau of Standards at the ice, steam and sulfur points. The ice point was determined in place after each assembly of the calorimeter. Thermometer resistances were measured with a G-2 Mueller bridge, and energy inputs with a White double potentiometer. A conventional adiabatic shield assembly and insulating jackets were provided.

Benzoic Acid.—The triple point of benzoic acid was determined to test the performance of the calorimeter. Table I
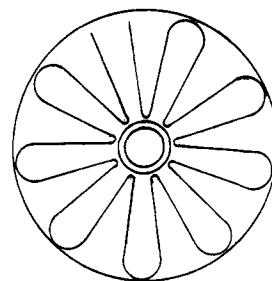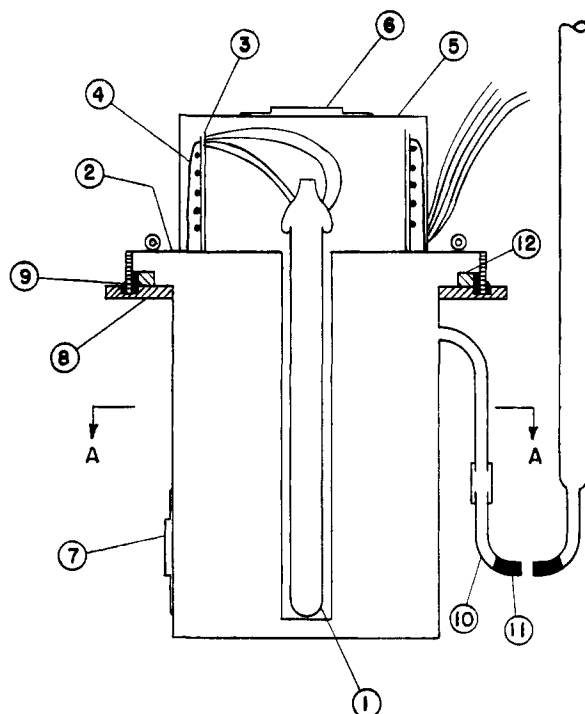

Section A–A

Fig. 1.—Calorimeter: 1, thermometer-heater; 2, calorimeter lid; 3, copper thermometer lead temperature equilibrating ring; 4, Sauereisen cement; 5, calorimeter top radiation shield; 6, attachment point for calorimeter to top shield difference thermocouple; 7, attachment point for calorimeter to side shield difference thermocouple; 8, brass flange; 9, soft solder seal; 10, evacuation tube; 11, soft solder seal; 12, brass ring.

lists the experimental equilibrium temperature, $t°$ (obs.), against experimentally determined reciprocal mole fraction melted, $1/x$. These data were fitted to a straight line by the method of least squares. Extrapolation to $1/X = 0$ yielded a value of 122.362° for the triple point of benzoic acid, checking exactly the value of Schwab and Wichers.[8] The sample used had a purity of 99.18 mole per cent.

Phthalic Anhydride

Difference between the Freezing Point and the Triple Point.

—The difference between the freezing point and the triple point, which includes the effect of dissolved air as well as the effect of pressure, was determined in a closed vessel provided with a mercury-filled thermometer well and a bubbler.

TABLE I
THE TRIPLE POINT OF BENZOIC ACID

t, °C. (calcd.)[a]	t, °C. (obsd.)	$1/X$	t, °C. (calcd. − obsd.)
121.188	121.187	1.9658	+0.001
121.429	121.431	1.5610	− .002
121.589	121.588	1.2933	+ .001
121.689	121.676[b]	1.1261	+ .013
121.754	121.754	1.0180	.000
122.362[c]		0.0000	

[a] Calculated from the least squares equation $t°C. = 122.362 − 0.05970/X$. [b] On account of the large deviation from the least squares line, this point was not used in the least squares treatment. [c] Triple point of benzoic acid calculated at $1/X = 0$.

(5)

(6) F. Lange, *Z. physik. Chem.*, **110**, 343 (1924).

(7) J. C. Southard and F. G. Brickwedde, THIS JOURNAL, **55**, 4378 (1933).

(8) F. W. Schwab and E. Wichers, *J. Research Natl. Bur. Standards*, **34**, 333 (1945).

The sample vessel had a volume of about 250 cc. The thermometer well was immersed to a depth of about seven inches. Phthalic anhydride was distilled directly into the vessel. The sample was melted and the vessel placed in a mineral oil-bath at 130.8°. Dry air was bubbled through the sample until the temperature was below the freezing point. Crystallization was induced by removing the vessel briefly from the bath to make negligible the amount of solid crystallizing due to supercooling. Time–temperature measurements were made until the temperature became constant. The sample was then degassed and the triple point determined in the same way. The amount crystallizing out during each run was about 3%, thus eliminating appreciable effects due to concentration of impurity.

The freezing point of this sample was 130.965°, the triple point, 130.953°. Thus the freezing point of phthalic anhydride is 0.012° higher than the triple point.

Triple Point.—Table II lists the melting data obtained on phthalic anhydride. By treating the data in the same way as with benzoic acid, the triple point of 100 mole per cent. phthalic anhydride

TABLE II

THE TRIPLE POINT OF PHTHALIC ANHYDRIDE

t, °C. (calcd.)[a]	t, °C. (obsd.)	$1/X$	t, °C. (calcd. − obsd.)
131.034	131.034	2.538	0.000
131.049	131.048	1.968	+ .001
131.056	131.056	1.671	.000
131.063	131.064	1.410	− .001
131.071	131.071	1.103	.000
131.100[b]		0.000	

[a] Calculated from the least squares equation t°C. = 131.100 = 0.0261/X. [b] Triple point of phthalic anhydride calculated at $1/X$ = 0.

was 131.100°. The maximum deviation of any point from the least squares straight line was ±0.001°. Because of the accumulation of errors in the different parts of the determination, the freezing point calculation is not considered to be accurate to better than 0.01°. Hence, the freezing point of pure phthalic anhydride, calculated from the above difference, is 131.11 ± 0.01°.

The triple point of the purified sample was 131.074°. The freezing point depression of 0.026° corresponds to an impurity of 0.05 mole per cent. After the determination of the triple point had been completed, the sample was poured directly into the Rossini apparatus and the freezing point determined with a cooling rate of 0.071° per minute. The temperature continued rising for 45 minutes after crystallization started, until it reached 131.-031°. At this point the stirrer jammed and the temperature immediately rose to 131.036°. Hence, it is demonstrated that even with this slow cooling rate, equilibrium is not established, the rate of crystallization increasing with the quantity of crystals present. With samples of lesser purity this continuous temperature rise would not be observed. Any increase in the rate of crystallization in the later stages of the determination, however, would tend to lessen the difference between the observed temperature and the equilibrium temperature. Hence, the sample would appear to be purer than it actually is. This probably accounts for the low results obtained by Debeau. The final temperature attained was about 0.05° lower than the freezing point of this sample.

Volume Change on Melting.—The change in volume on melting was measured in a simple mercury dilatometer. The value obtained for this quantity is 19.6 cc. per mole. Using this value, the change in triple point with pressure calculated

TABLE III

EFFECT OF PROBABLE IMPURITIES ON THE FREEZING POINT OF PHTHALIC ANHYDRIDE

Impurity A[a]	Impurity B[a]	A, moles	B, moles	Moles PAA	Mole frac. PAA	ΔT (calcd.)[b]	ΔT (found)
			Series A				
MAA	...	0.00768	.....	0.625	0.9879	0.72	0.68
NQ	...	.00475	.....	.573	.9918	.49	.59
PA	...	.00452	.....	.567	.9921	.47	.47
MA	...	.00631	.....	.615	.9899	.60	1.12
FA	...	.00088	.....	.598	.9986	.09	0.14
PI	...	.00506	.....	.943	.9947	.32	.46
BA, FA, MAA, NQ, PI, PA	...	.00556	.....	.558	.9901	.59	.68
			Series B				
BA	...	0.00694	.....	0.594	0.9884	0.68	0.64
PA	BA	.00213	0.00289	.844	.9941	.34	.23
PA	BA	.00213	.00290	.507	.9902	.58	.42
PA	FA	.00088	.00091	.594	.9970	.18	.16
PA	PI	.00214	.00242	.540	.9916	.48	.45
FA	BA	.00087	.00128	.716	.9970	.17	.19
BA	PI	.00291	.00243	.527	.9900	.58	.55
FA	PI	.00087	.00103	.560	.9966	.19	.20
MAA	BA	.00290	.00379	.540	.9878	.71	.74
MAA	PI	.00353	.00241	.547	.9893	.62	.69
MAA	FA	.00087	.00168	.574	.9956	.26	.25

[a] BA = benzoic acid, FA = fumaric acid, MA = maleic acid, MAA = maleic anhydride, NQ = 1,4-naphthoquinone, PA = phthalic acid, PAA = phthalic anhydride, PI = phthalimide. [b] Calculated from the equation, $\log N_1 = \Delta H/2.3R$ $(1/T_1 - 1/T_0)$.

from the Clapeyron equation is 0.033 ± 0.001°/ atm. However, the difference between freezing and triple point as reported above is only 0.012°. The difference of 0.021° results from the solubility of air, which, if Raoult's law is obeyed, amounts to 0.04 mole per cent.

Effect of Impurities on the Freezing Point of Phthalic Anhydride.—The effects of various probable impurities on the freezing point of phthalic anhydride determined in the Rossini apparatus are listed in Table III, singly, in pairs, and finally, all seven together. The amount of fumaric acid which could be added was limited because of its low solubility in molten phthalic anhydride. Maleic acid dehydrated, resulting in twice the freezing point depression calculated from the quantity added.

The freezing points of all the mixtures, except that in which both benzoic acid and phthalic acid were present as impurities, agreed with calculated values within experimental error. In this case the depression was only 0.70 of the calculated value. Because of this discrepancy, the melting behavior of this mixture was investigated in the calorimeter. Table IV lists the melting data obtained on this mixture. The points (first three in

TABLE IV

PHTHALIC ANHYDRIDE WITH PHTHALIC ACID AND BENZOIC ACID ADDED AS IMPURITIES

t, °C. (calcd.)[a]	t, °C. (obsd.)	$1/X$	t, °C. (calcd. − obsd.)
128.464	128.737	5.126	−0.273
129.416	129.495	3.338	− .079
129.691	129.733	2.822	− .042
130.136	130.136	1.985	.000
130.284	130.279	1.708	+ .005
130.423	130.432	1.446	− .009
130.545	130.540	1.217	+ .005

[a] Calculated from the least squares equation $t°C. = 131.93 − 0.5324/X$, obtained by treating only the last four points.

Table IV) at low fraction melted, deviate from the linearity of the points (last four in Table IV) at high fraction melted. Hence, they were left out of the least squares treatment. This type of behavior is characteristic of systems in which there is solid solution formation. The experimental triple point depression, ignoring solid solution formation by neglecting the mentioned points, was 0.75 of the value calculated assuming Raoult's law and a liquid-soluble, solid-insoluble impurity.

GLENOLDEN, PENNA.

Polymorphism of Sodium Superoxide

BY GILES F. CARTER AND D. H. TEMPLETON

The structures of sodium superoxide have been studied by powder and single crystal X-ray diffraction methods at low temperatures. NaO_2 (I) stable above −50°, has a disordered pyrite structure, with $a = 5.49$ Å. at 25°. The disorder probably is dynamic. NaO_2 (II) exists from −50 to −77° with the pyrite structure, with $a = 5.46$ A. at −70°. The oxygen parameter is $u = 0.43$. NaO_2 (III) exists below −77° with the marcasite structure, space group Pnnm, with $a = 4.26$ Å., $b = 5.54$ Å. and $c = 3.44$ Å. at −100°. The oxygen parameters are $x = 0.12$ and $y = 0.43$.

Previous work in this Laboratory[1] has shown that the crystal structure of sodium superoxide, NaO_2, at room temperature is similar to that of sodium chloride. The superoxide ion, O_2^-, is located at the anion position with rotational disorder. A search by the X-ray diffraction technique for low-temperature ordered forms, suggested by this disorder, has revealed two whose structures are described in the present paper. Single crystal X-ray diffraction data have also yielded more detailed information concerning the angular distribution of the rotation of the superoxide ion at room temperature.

We designate the three forms of sodium superoxide as I, II and III in decreasing order of temperature ranges of stability. Todd[2] has observed peaks in the heat capacity curve at 196.5 and 223.3°K. which correspond to the transition temperatures which we determine less accurately by the X-ray experiments. Zhdanov and Zvonkova[3] reported

unit cell dimensions for $NaO_2(I)$ and $NaO_2(II)$ (which they designated as β and α, respectively) which are not in good agreement with our results. They also observed that sodium superoxide tends to become antiferromagnetic at the transition I → II.

Experimental

Sodium superoxide and potassium superoxide samples were provided by Dr. John L. Margrave. Single crystals of sodium superoxide of cubic habit (about 0.1 to 0.3 mm. on an edge) were obtained by slow evaporation of a liquid ammonia solution. Previous attempts to grow crystals by fusion and slow cooling failed because of decomposition. The crystals or powdered samples were sealed in Pyrex capillaries under an atmosphere of argon dried with molten sodium. For the low temperature photographs, the samples were cooled by a stream of nitrogen produced by electrical evaporation of the liquid. The temperature was measured by a thermocouple near the sample with an accuracy estimated as ±5°. Powder and Weissenberg photographs were taken in cameras of radius 2.86 cm. with Cu $K\alpha$, X-rays, $\lambda = 1.5418$ Å. Intensities were estimated visually by comparison with spots made with a set of exposure times.

Crystal Structure of NaO_2 (I).—In the previous work[1] four different models of the rotational disorder were considered: (1) orientation parallel to the three axial directions, (2) spherical symmetry, (3) orientation parallel to the four

(1) D. H. Templeton and C. H. Dauben, THIS JOURNAL, 72, 2251 (1950).

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(3) G. S. Zhdanov and Z. V. Zvonkova, Doklady Akad. Nauk S. S. S. R., 82, 743 (1952); read only in abstract form, C. A., 46, 6893 (1952).