since the oxygen content of CeS is reduced by heating with excess cerium. However, since cerium metal usually contains appreciable amounts of cerium carbide, the removal of the oxide impurity might be due to CO formation.

If CeS with a very low Ce_3S_4 content is heated with a small amount of Ce_2O_2S above 1700° in a vacuum, CeO should be evolved as a gas and Ce_3S_4 should be produced as a liquid or solid. This reaction should proceed until the activity of the Ce_2O_2S has been reduced to a low value, by virtue of its solution in the Ce_3S_4 produced in the reaction. Experimentally it has been found necessary to add metallic cerium in order to obtain any appreciable reduction of oxygen content in CeS through volatilization of CeO.

Except for the previously mentioned change of crystal structure of Ce_2S_3 by the presence of Ce_2O_2S, there appears to be no reaction of the thio-oxide with Ce_3S_4 or Ce_2S_3.

Thorium, Uranium and Zirconium.—As with cerium, the oxide-sulfides of these elements can be completely converted to the highest sulfides by H_2S in a graphite system at about 1500°. It has been reported[12] that ThOS reacts with carbon at about 1900° producing ThS and CO and although no other products were noted, the resulting material undoubtedly contained thorium carbide and oxide in addition to the sulfide. Metallic thorium reacts with ThOS forming ThS and ThO_2.

From the experimental evidence that ThO_2 is stable when heated with ThS, the most probable reaction of ThS with ThOS is the formation ThO_2 and Th_2S_3. With the higher sulfides, Th_4S_7 and ThS_2, the sulfoxide does not react. The stability of ThOS in the presence of Th_2S_3 is not known but it is suspected that it exists under such conditions.

Thermochemistry

Cerium.—Although the heat of solution has not been determined for the thio-oxide and, therefore, the heat of formation has not been directly determined, some estimates of this latter quantity can be made from the following considerations. In a transpiration experiment during the course of the work, nitrogen was bubbled through liquid sulfur at a temperature for which the vapor pressure of sulfur is about 0.1 atm. and then was passed over powdered CeO_2 in a furnace at a temperature of about 1500°. In about two hours with a nitrogen flow of about one ml./sec. essentially complete conversion to Ce_2O_2S had occurred but conversion to the sesqui-sulfide was not attained. In a graphite apparatus conversion to Ce_2S_3 has been obtained in long runs as low as 1300°K. and in four hours at about 1600°K. These experiments allow estimation of equilibrium constants which when combined with estimated entropies give limits on the heat of formation of the thio-oxide. If the heat of formation of Ce_2S_3 from rhombic sulfur is taken as $\Delta H_{298} = -300.5$ kcal./mole and if the heat of formation of CeO_2 is taken as $\Delta H_{298} = -448$ kcal./mole, our estimate for the heat of formation of Ce_2O_2S is $\Delta H_{298} = -430 \pm 15$ kcal./mole from rhombic sulfur.

Thorium.—Our estimate for the heat of formation of ThOS at 1500°K. based upon similar considerations is $\Delta H = -210 \pm 20$ kcal./mole.

It is interesting to note that sulfides of both the two and three oxidation states are quite stable for all the elements discussed in this paper while except for the tripositive oxide and thio-oxide of cerium, none of these elements has stable oxides or oxide-sulfides of the two and three oxidation states. This difference is general for most metallic elements and appears to be due mainly to the greater decrease in stability of lattices of higher oxidation number than of the lattices of lower oxidation number when the oxide ions are replaced by sulfide ions. This is due to the considerable anion–anion repulsion introduced when one tries to crowd the large sulfide ions around a small metallic ion.

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[12] B. M. Abraham and N. R. Davidson, Manhattan District Paper CN-3001, May, 1945.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

α-Halo Ketones. III. Solid–Liquid Equilibrium in the System 2-Chloro-3-heptanone and 4-Chloro-3-heptanone[1]

BY J. D. NEWKIRK AND J. G. ASTON

The solid–liquid equilibrium diagram for the system 2-chloro-3-heptenone (B) and 4-chloro-3-heptanone (A) has been determined. Compounds A_3B_2 and AB are formed, the former, being unstable, giving a peritectic point.

In the present paper is presented the solid–liquid equilibrium phase diagram for the system 4-chloro-3-heptanone and 2-chloro-3-heptanone which has been determined experimentally for later use in ascertaining the composition of the product resulting from the direct chlorination of 3-heptanone.

Experimental

Preparation of Materials.—Both chloroketones were prepared by the method of Cason[2a,2b] whereby a chloroacid chloride is coupled with a cadmium alkyl. The compounds were fractionated through a column of about 20 theoretical plates. Purities and heats of fusion for both isomers were determined in a calorimeter type melting point apparatus developed by Aston and co-workers.[3]

The calorimetric data thus obtained assuming solid insolubility of the impurity, indicated that for 4-chloro-3-heptanone ΔH_f = 3092 cal./mole, T_0 = 212.05°K. and 96.02% purity, while for 2-chloro-3-heptanone ΔH_f = 3613 cal./mole, T_0 = 225.90°K. and 95.19% purity, where ΔH is the heat of fusion and T_0 the melting point of the pure compound calculated from the data.

Although the purities were low in both cases, lack of material and difficulty in crystallization prevented further purification by fractional crystallization.[3]

Apparatus and Method.—The phase diagram is shown in Fig. 1 and the data from which it was constructed in Table I.

TABLE I

COMPOSITION AND TEMPERATURE OF POINTS ON PHASE DIAGRAM

Point	Composition, mole % B	Liquidus point, °C.
1	0	210.22
2	9.09	207.67
3	23.1	203.18
4	33.3	205.95
5	41.2	210.06
6	47.4	210.58
7	53.5	210.58
8	62.2	213.72
9	50.0	210.87
10	55.6	210.99
11	62.5	213.71
12	71.5	216.61
13	83.4	219.92
14	100	224.21

The data assembled for the phase diagram were deter-

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[1] The first two papers were: I, Aston and Greenburg, THIS JOURNAL, **62**, 2590 (1940); II, Greenburg and Aston, *ibid.*, **62**, 3135 (1940).

[2] (a) Cason, *ibid.*, **68**, 2078 (1946); (b) Aston and Newkirk, *ibid.*, **73**, 3900 (1951).

[3] Aston, Fink, Tooke and Cines, *Ind. Eng. Chem., Anal. Ed.*, **19**, 218 (1947).

mined in a Rossini melting point apparatus[4] because crystallization could not be induced in the calorimeter employed for the purity determinations.

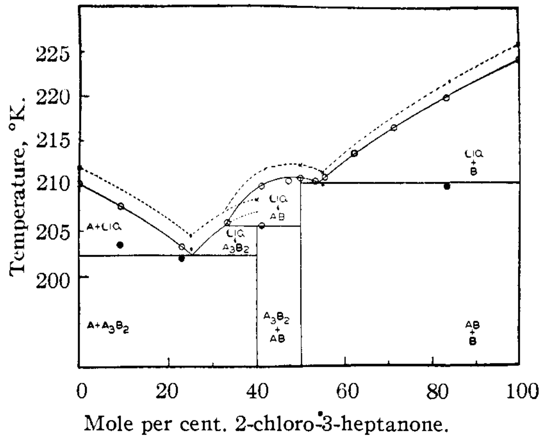

Fig. 1.—Solid–liquid equilibrium diagram for the system 4-chloro-3-heptanone (A) and 2-chloro-3-heptanone (B).

The temperature was determined by means of a strain free platinum resistance thermometer of the type described by Myers.[5]

To measure the resistance a Leeds and Northrup type K-2 potentiometer was used to measure the potential across the thermometer and a 100-ohm standard resistor in series with it. A thermometer current of approximately 1 milliampere was used. The Rubicon enclosed lamp and scale galvanometer sensitive to about 0.2 microvolt allowed the temperature to be read to 0.005°.

At all times a slow stream of dry nitrogen was maintained over the solutions. Potential readings were taken every two minutes in the solid region and every minute in the region where stirring was possible and extended well into the completely liquid region, the almost constant current readings for each point being determined by interpolation.

The warming curves were prepared by plotting potential as ordinates *versus* time as abscissas. From the warming curves, the eutectics of compound AB with 2-chloro-3-heptanone (B) and of 4-chloro-3-heptanone (A) with compound A_3B_2 were found by examining the curves and noting an abrupt change in slope occurring when the eutectic had completely melted. The eutectics should show a flat portion in the warming curve if there were no impurities. However, since the isomeric chloroketones were prepared from different starting materials, the impurity is obviously different in each case so that on admixture of the one isomer with the other a four component system is produced. Thus in the first part of the warming curve there is a liquid solution of all four components in equilibrium with 4-chloro-3-heptanone and 2-chloro-3-heptanone. The change in slope when one of them disappears is easily discernible and is apparent from perusal of the warming curves. This point corresponds to the eutectic temperature as lowered by the two minor components.

In the region where compound A_3B_2 decomposes, the temperature remains essentially constant until this transition is completed (peritectic point). The temperature then abruptly rises several degrees and flattens off again, until melting is completed. A warming curve for point 5 on the phase diagram is included as an illustration in Fig. 2.

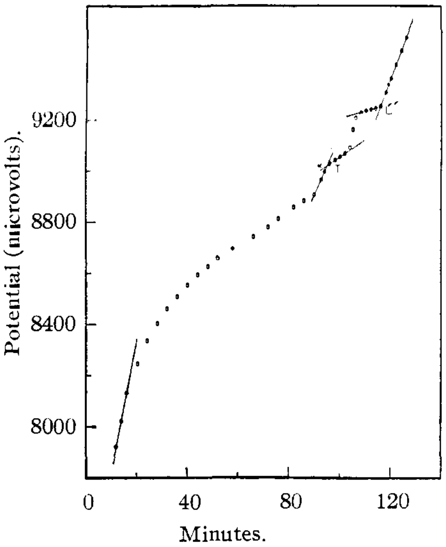

Fig. 2.—Typical warming curve.

A straight line was drawn, at the end of the liquid–solid region, where the potential varied linearly with respect to time. Similarly the completely liquid points were extrapolated. The lines so drawn intersected at the liquidus point. The resistance corresponding to the potential at the breaks was calculated from the interpolated current.

The point corresponding to the transition of A_3B_2 is marked T on the warming curve and is denoted on the phase diagram as a half-darkened circle. The time when stirring was started is indicated by an asterisk. The liquidus point is marked L.

The compositions were calculated assuming pure compounds. The eutectic temperatures and compositions were calculated by the following expressions for the freezing point of ideal solutions

$$\ln\frac{1}{N_a} = \frac{\Delta H_{f_a}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \qquad (1)$$

for one constituent with mole fraction N_a and

$$\ln\frac{1}{1 - N_a} = \frac{\Delta H_{f_b}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \qquad (2)$$

for the other constituent with mole fraction $1 - N_a$.

Before applying the equations above, T_0 corresponding to the melting point of the pure compounds A_3B_2 and AB, respectively, were calculated. This was done by considering that all liquidus points, *i.e.*, freezing points, had been depressed by an amount corresponding to the impurities present in the original components, given by the expression

$$X = \frac{\Delta H_f}{R}\left(\frac{1}{T_{100}} - \frac{1}{T_0}\right) \qquad (3)$$

where X is the mole fraction of impurity, calculated from the impurity in the components, and where T_{100} is the temperature corresponding to the liquidus point for AB and in the case of A_3B_2 the temperature of melting of A_3B_2 obtained by extrapolation. The T_0 for 2-chloro-3-heptanone and 3-chloro-3-heptanone were those obtained calorimetrically. The necessary value of ΔH_f for each of the compounds A_3B_2 and AB was calculated from those of

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(4) Rossini, *Bur. Standards J. Research*, **26**, 591 (1941).

(5) Myers, *ibid.*, **9**, 807 (1932).

the components by assuming it a linear function of the composition, *i.e.*, the heat of formation of the compound was zero. The value of T_0 thus calculated along with the experimentally determined melting points of the four substances are given in the last column of Table II.

Table II

Melting Points and Eutectic Points

Compound	T_{100} experimental, °K.	T_0 (calcd.), °K.
4-Chloro-3-heptanone (A)	210.2	212.05[a]
A_3B_2	207.2	208.60
Eutectic of A with A_3B_2 comp. 25.4% B	202.3	204.45 (25% B)
AB	211.0	212.47
Eutectic of AB with B comp. 54.2% B	210.4	211.6 (55% B)
2-Chloro-3-heptanone (B)	224.2	225.90[a]

[a] From calorimetric data

From the data obtained as above a temperature of 204.45° and composition of 25% total per cent. B of the eutectic formed between 4-chloro-3-heptanone and compound A_3B_2, undepressed by the presence of any impurity was calculated. Similarly T_0 of the eutectic formed from AB with 2-chloro-3-heptanone was determined as 211.6° at 55 total per cent. B. These points are marked on the phase diagram Fig. 1, as asterisks, as are the melting points of the original components and the compounds A_3B_2 and AB. These points on connection as shown by the dotted curve yield a representative phase diagram for pure components A and B.

The eutectic points, depressed by the presence of the known amounts of impurities, were calculated as 203.03 and 210.18°, respectively, and are denoted by (+) immediately below those denoting the pure eutectics. The lowering of the eutectic point was calculated using equation (3), where X is the mole per cent. of total impurity other than the two chloroketones and

$$\Delta H_f = N_A \Delta H_{f_A} + N_B \Delta H_{f_B}$$

where N_A and N_B are the mole fractions of the two chloroketones and ΔH_{f_A} and ΔH_{f_B} are their heats of fusion.[6]

Theoretically these points should agree with the eutectics plotted on the phase diagram as determined from the warming curves. The eutectic temperatures and the melting points of the compounds A_3B_2 and AB obtained from the phase diagram (Fig. 1), uncorrected for lowering, as well as the melting points of A and B obtained from the warming curves, without correction for impurity, are given in the second column of Table II.

[6] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., p. 240, Exercise 3.

State College, Penna. Received January 16, 1950

[Contribution from the School of Chemistry and Physics, The Pennsylvania State College]

α-Halo Ketones. IV. The Isomeric α-Chloroketones Derived from 3-Heptanone

By J. G. Aston and J. D. Newkirk

A suitable resonance intermediate has been proposed to explain rearrangements during metathesis of α-haloketones which predicts the same products from the two α-isomers. The preparation of 4-chloro-3-heptanone is described for the first time. The product of chlorination of 3-heptanone consists of 74% of the 2-chloro and 26% of the 4-chloro isomer as determined by a warming curve. The product obtained from both isomers by the action of anhydrous sodium methylate in ether is the methyl ester of 2-ethylvaleric acid. It has not been possible to ascertain the composition of the chlorination or bromination product of isopropyl isobutyl ketone.

The investigation of McPhee and Klingsberg[1] has done much to clarify the theoretical basis of the rearrangement of α-haloketones to esters by the action of sodium alcoholates and to acids by the action of sodium hydroxide. A more general formulation of their mechanism is shown.

In this scheme IIIra, IIIrb are the two resonance forms arising separately by ionization of the keto and enol forms of the fragment derived from I by loss of X^-, while IIIrc and IIIrd are the corresponding forms derived from III. However, there is no assumption made concerning the initial point of attack which may be by the removal of X^- or by the removal of H^+. The significant assumption is that the reaction intermediate in the rearrangement is stabilized by resonance between four forms and this may explain the preference for rearrangement over direct replacement which presumably involves an intermediate of the type $\overset{-}{Y}\overset{+}{R}\overset{-}{X}$. The ester (or acid) finally obtained is that at the end of the most favorable path.

The reaction of aqueous sodium hydroxide on α-haloketones usually produces replacement of halogen by hydroxyl. If this replacement also involves the common intermediate III, the same hydroxy ketone will result from I and II, namely, that most readily derived from III. *Since the structure of α-bromoketones as obtained by bromination has hitherto been assigned on the basis of the products of hydrolysis*[2] we are left with no certain knowledge of which α-carbon atom is substituted when a ketone is halogenated.

In order to ascertain the nature of the chlorination product of 3-heptanone, 2-chloro- and 4-chloro-3-heptanone have been synthesized by the reaction of the appropriate cadmium alkyl on the required chloro acid chloride using the method devised by Cason.[3]

The solid equilibrium diagram has been previously determined from warming curves on mixtures of these isomers.[4] By taking the warming

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[1] McPhee and Klingsberg, This Journal, **66**, 1132 (1944).

[2] Favorskii, *J. prakt. Chem.*, [2] **88**, 641 (1913).

[3] Cason, This Journal, **68**, 2078 (1946).

[4] Newkirk and Aston, *ibid.*, **73**, 3898 (1951).