

**754.** *A New Twin Micro-calorimeter, and the Heat of Transformation of  $\alpha$ - into  $\beta$ -Quinol.*

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A new twin micro-calorimeter is described, in which differential or direct heats of solution can be measured accurately. The calorimeter is vacuum- and pressure-tight, and the solutions come into contact with glass surfaces only. The heat of solution of potassium chloride in water has been measured. The preparation of  $\beta$ -quinol is described, and the heat of formation from  $\alpha$ -quinol measured. For  $\alpha$ -quinol (solid)  $\longrightarrow$   $\beta$ -quinol (solid),  $\Delta H = 0.13 \pm 0.03$  kcal./mole.

QUINOL exists in three crystalline modifications, referred to as the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -forms; the  $\alpha$ -form is the common one.  $\beta$ -Quinol can be obtained under special conditions from alcoholic solutions (see p. 3935) and is the modification which forms the lattice cage in the "clathrate" compounds described by Palin and Powell (*J.*, 1948, 815).  $\gamma$ -Quinol can be obtained by sublimation of  $\alpha$ -quinol.

The heat of the transition of  $\alpha$ - into  $\beta$ -quinol has now been measured, so that when this is combined with heats of formation of clathrate compounds relative to  $\alpha$ -quinol, the interaction energies of the enclosed molecules with the cage can be evaluated. The heat of the transition also provides information about the relative stabilities of the  $\alpha$ - and the  $\beta$ -form of quinol. The measurements on the clathrate compounds themselves will be published shortly.

For the present measurements a twin calorimeter has been constructed which can be used to determine heats of solution or reaction of a wide range of substances. The solutions are in contact with glass surfaces only, so that corrosive or organic solvents can be used freely, and each calorimeter is pressure- and vacuum-tight. The calorimeter can be used for differential measurements, as in this research, in which electrical energy is used to compensate for the difference in the heat of solution of two substances when dissolved one in each calorimeter, or for direct measurements, also using electrical compensation. The maximum sensitivity is such that temperature differences between the two calorimeters of about  $1 \times 10^{-6}^\circ$  can be observed. Only very small quantities of solute are therefore required.

## EXPERIMENTAL

*Calorimeter.*—The twin calorimeter (Fig. 1) consists of two similar Dewar vessels, supported from a flat brass plate in such a way that the joints between the plate and calorimeters are vacuum- and pressure-tight. Each calorimeter has inside it a stirrer, a sample-bulb holder and breaker, a calibrated electric heater, and two thermels. These project into the calorimeters from the top plate through vacuum- and pressure-tight seals. The whole assembly is immersed in a thermostat held at  $25.00^\circ \pm 0.003^\circ$ .

*Dewar Vessels.*—The calorimeters, *A*, *A'*, have a capacity of 500 c.c. and are made as nearly identical as possible. The top of each Dewar vessel is flanged and ground to a flat surface. Rubber gaskets are cemented to the flanges and also to the brass plate with Bostik cement. Each calorimeter is supported from the bottom by means of a cork cup, *C*, glued to a brass plate. This slides over tapped brass rods, *B*, projecting down from the top plate, and with the aid of thumb-screws enables the calorimeter to be pressed tightly into position. The heat capacities of the calorimeters when filled with the normal charge of about 300 c.c. of water differ by 0.15%, and a correction for this is accordingly applied. The difference in the heat capacities was determined by passing a known amount of electrical energy through the heaters wired in series. The small temperature difference between the two calorimeters was then reduced to zero by applying more heat through the appropriate heater. Errors due to this small difference in heat capacities could also be virtually eliminated by repeating each measurement in alternate calorimeters.

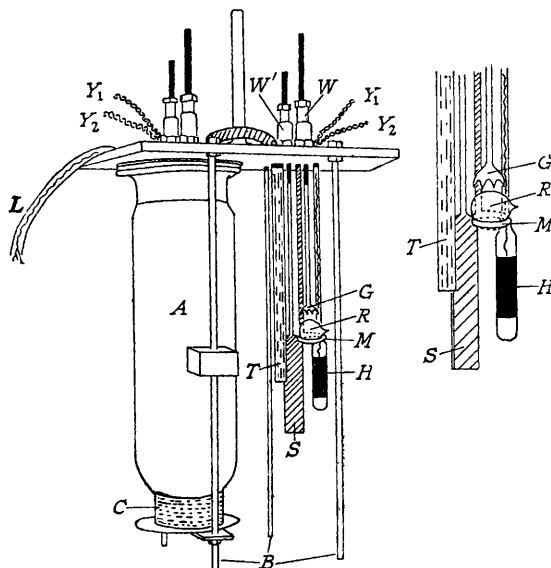
*Bulb Holders and Breakers.*—The samples are sealed into thin-walled glass bulbs, *R*, about 2 cm. in diameter, after the latter has been filled with dry air. The sample bulb rests on a glass ring, *M*, supported by a glass rod from the top plate. A glass claw, *G*, holds the bulb in place

from above, and prevents it from floating in the surrounding liquid. The claw is at the end of a thin glass tube which is waxed to a stainless-steel rod just below the surface of the top plate. The steel rod passes through a Wilson-type vacuum seal, *W* (Wilson, *Rev. Sci. Instr.*, 1941, 12, 91), attached to the top plate, and when the rod is depressed, the sample bulb is broken and thrust completely through the supporting ring. This ensures that the solute dissolves as quickly as possible.

*Thermels.*—There are two thermels, *T*. The main one indicates the temperature difference between the two calorimeters, and the subsidiary one indicates the temperature difference between one of the calorimeters and the surrounding bath. The main thermel consists of 19 chromel–constantan junctions and one copper–constantan junction, the last to avoid external thermal E.M.F.s. The relative diameters of the chromel and constantan wires are chosen to give the maximum ratio of electrical to thermal conductivity, and are 24 and 26 s.w.g., respectively. Since a limiting factor in the design of the thermel is the heat conducted along the wires, it is possible to assign a factor of merit, *m*, to different combinations of thermocouple materials, which is identical with that obtained by Hornig and O’Keefe (*ibid.*, 1947, 18, 474) for radiation thermocouples. This is given by  $m = E/(\sqrt{k_1 r_1} + \sqrt{k_2 r_2})$ , where *E* is the thermoelectric

FIG. 1.

- A*, Dewar vessel.
- B*, tapped rods.
- C*, cork support.
- G*, bulb breaker.
- H*, heater.
- L*, output leads.
- M*, bulb holder.
- R*, sample bulb.
- S*, stirrer.
- T*, thermels.
- W* and *W'*, “Wilson” seals.
- Y*<sub>1</sub> and *Y*<sub>2</sub>, current and potential leads.



power of the junction,  $k_1$  and  $k_2$  are the thermal conductivities of the two wires, and  $r_1$  and  $r_2$  are the electrical resistivities. The choice of chromel–constantan junctions was determined by the ready availability of these wires coupled with a relatively high factor of merit, *m*.

The thermel junctions are insulated with Bakelite varnish and embedded in naphthalene at the bottom of the thin glass sheaths. Each junction is pressed tightly against the flat bottom of its sheath. The connecting wires which pass over the top of the brass plate from one calorimeter to the other are insulated from the water by a liberal coating of beeswax–resin mixture. The copper output leads, *L*, are connected through a resistance network to a photoelectric galvanometer amplifier, using negative feedback, similar to the one described by Preston (*J. Sci. Instr.*, 1946, 23, 173). The resistance network is wired on a wafer switch immersed in oil in a well-lagged metal box. This enables the sensitivity of the detecting system to be varied stepwise by means of series resistances, and also the amplifier can be switched to a manganin resistance equal in value to that of the thermel, in order to check the zero position. All leads were electrically screened by earthed braiding. The sensitivity of the amplifier is normally adjusted so that 1 mm. deflection of the secondary galvanometer corresponds to a temperature difference between the two calorimeters of  $4 \times 10^{-6}^\circ$ .

The subsidiary thermel consists of four chromel–constantan junctions, and is connected to a galvanometer. Its sensitivity is such that 1 mm. deflection of the galvanometer corresponds to a temperature difference between the calorimeter and the bath of  $0.001^\circ$ .

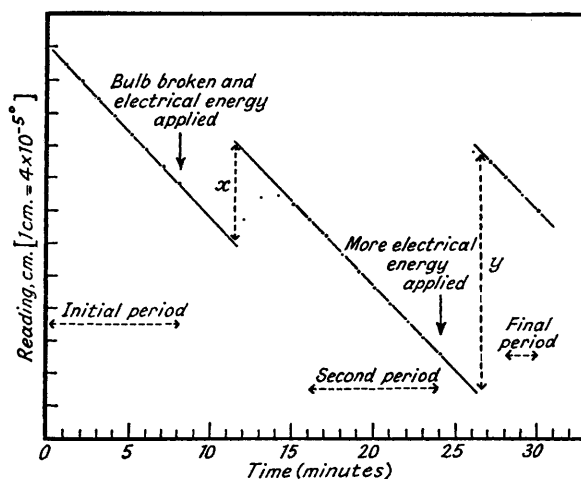
*Stirrers.*—These are of the paddle type, and consist of similar pieces of sheet Pyrex glass, *S*,

fused to narrow glass tubes. The glass tubes are waxed to stainless-steel rods just below the top plate, and the steel rods pass through Wilson seals, *W'*, lubricated with silicone grease. The stirrers are driven at identical speeds (about 150 r.p.m.) by means of flexible cables connected to either end of a single shaft of a reduction gear driven by a synchronous motor.

*Heaters.*—The heaters, *H*, of resistance approximately 92 ohms, are wound with 40 s.w.g. Eureka wire on a varnished cylinder of copper foil. The heater coil is wrapped with aluminium foil and coated with Bakelite varnish. Current and potential leads,  $Y_1$ ,  $Y_2$ , are soldered to the coil, and the resistances of the two are adjusted to be the same to within 0.03%. The entire assembly is enclosed tightly in a glass sheath (thickness, *ca.* 0.25 mm.), and the leads pass through a tube which is cemented into a tight-fitting hole in the brass plate. The resistances of the heaters are measured potentiometrically under working conditions, a Tinsley Vernier potentiometer being used. They can also be checked at any time with the current-standardising arrangement.

The amount of electrical energy supplied to the heaters is measured by means of a simple potentiometric arrangement similar to that described by Westrum and Robinson ("Transuranium Elements," Part II, National Nuclear Energy Series). In this arrangement, the current flowing through the heaters and a standard resistance is maintained at a fixed value by balancing

FIG. 2.



the potential drop across the standard resistance against a Weston cell. The heater current can be switched to a dummy load or to either calorimeter, and the time during which the current flows through a calorimeter is measured by a stop-watch reading to 0.02 sec. which is mechanically linked to the switch.

*Procedure.*—Almost equal amounts of  $\beta$ -quinol and  $\alpha$ -quinol (about 90 mg.) are weighed into thin-walled glass bulbs, which are sealed off in a dry atmosphere and mounted in the holders. Equal volumes of solvent at about the correct temperature are run into each Dewar flask, from a constant-volume pipette, and the calorimeters are screwed tightly into place. The whole assembly is mounted in the thermostat, and the calorimeters are brought to the same temperature as the bath to within about 0.005°, the subsidiary thermel and the calorimeter heaters being used. The calorimeters are then allowed to reach equilibrium, and a linear drift in the temperature difference between them is obtained: this usually takes about 0.5 hour. This drift, which is largely due to inequalities in the heats of stirring, is usually between 10 and  $25 \times 10^{-60}$  per minute. The sample bulbs are then broken simultaneously, and a known amount of electrical energy supplied to compensate for the temperature difference set up. When both samples have dissolved completely, the new reading of the main thermel is plotted for several minutes. A further known amount of electrical energy is then supplied, and a third set of thermel readings taken. A typical graph is shown in Fig. 2. If  $Q_1$  and  $Q_2$  are the respective amounts of heat supplied, then the difference,  $Q$ , in the heat changes in the two calorimeters, is given by  $Q = Q_1 + (x/y)Q_2$ . If both Dewar vessels change in temperature by only small amounts as in these experiments, the initial and final slopes of the temperature-time graph are almost

equal, and there is no difficulty in extrapolation. If the temperature changes are much larger, then the initial and final slopes are appreciably different, owing to the slightly different heat losses of the two Dewar vessels. A correction may then be applied by extrapolating the final slope to a point corresponding to the start of the reaction. This involves the assumption that the bulk of the sample dissolves rapidly, as was in fact the case in all these experiments. The errors introduced are very small unless the time of solution is particularly long. This procedure also eliminates errors which might be caused owing to changes in the heat of stirring brought about by the breaking of the bulbs. Corrections which arise from the fact that the two Dewar vessels are not kept at exactly the same temperature whilst the samples are dissolving, can be shown to be less than 0.1% of the heat of solution from a knowledge of the observed temperature differences, and the thermal leakage coefficients of the calorimeters (approx. 0.001°/min./degree). A correction for the heat of breaking a bulb is unnecessary, as bulbs of closely similar volumes are always used. The heat of breaking an empty bulb filled with dry air is about  $-0.05$  cal. ( $1.7 \times 10^{-4}$ ). This absorption of heat is largely due to the expansion of water vapour into the dry air.

*Heat of Solution of Potassium Chloride.*—In order to test the accuracy and reproducibility of the calorimeter, the heat of solution of potassium chloride in water has been measured. The results obtained for the reaction  $\text{KCl (solid)} + 6000\text{H}_2\text{O} = \text{KCl}, 6000\text{H}_2\text{O}$  at 25° are shown below :

Run no. ....	1	2	3	4	Mean
$\Delta H$ , cal. ....	+4159	+4162	+4157	+4158	$4159 \pm 3$ cal. = $17,400 \pm 10$ abs. joules

The potassium chloride was an "AnalaR" sample, twice recrystallised from water, dried in an oven, and finally heated for some time just below the melting point to remove the last traces of water. The value of this heat of solution, interpolated from the data given in "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, 1950, is +4151 cal.

*Preparation of Quinol Samples.*— $\alpha$ -Quinol. Commercial quinol was recrystallised once from water and once from ethyl alcohol, dried in a vacuum-desiccator, and finally heated at 150° for some time to ensure the absence of  $\beta$ -quinol and solvent. Analysis by titration with ceric sulphate solution (Kolthoff and Lee, *Ind. Eng. Chem., Anal.*, 1946, 18, 452) gave a purity of 99.9—100.0%.

$\beta$ -Quinol. The first attempts to prepare  $\beta$ -quinol were made by the method of Powell and Riesz (personal communication), in which quinol is recrystallised from alcohol at  $-78^\circ$ . The samples obtained gave X-ray powder photographs characteristic of  $\beta$ -quinol, but when they were dissolved in water, a gas was evolved. The gas contained 28% of oxygen and the rest was apparently nitrogen. It seems likely, therefore, that this substance is in fact an "air" clathrate compound. The total volume of gas evolved from a known weight of sample was measured with a nitrometer, and corresponded to approximately 12% of the available spaces filled in the  $\beta$ -quinol lattice.

It was found that  $\beta$ -quinol, free from enclosed gases, can be conveniently prepared by recrystallisation from ethyl alcohol under controlled conditions. A solution of quinol in ethyl alcohol is boiled for some time to remove air and  $\alpha$ -quinol nuclei, and the container tightly stoppered.  $\beta$ -Quinol crystallises out on cooling. Ethyl alcohol seems to be specific for this purpose, since water, *n*-propyl alcohol, *n*-butyl alcohol, and ether under similar conditions all give  $\alpha$ -quinol. Several calorimetric measurements were carried out on samples prepared in this way, but on analysis the  $\beta$ -quinol was found to contain 0.7—0.9% of ethyl alcohol, which was tenaciously retained, even under rotary-pump vacuum for prolonged periods. It is possible that, although the ethyl alcohol molecule is too large to form a normal clathrate compound, yet small amounts can be accommodated in the  $\beta$ -quinol lattice.

Almost pure  $\beta$ -quinol (99.8% with respect to ceric sulphate) was finally prepared by recrystallisation of quinol from air-free *n*-propyl alcohol in the presence of a seed of argon clathrate compound. The crystals deposited were filtered off, and dried in a vacuum-desiccator. Since  $\beta$ -quinol tends to change into  $\alpha$ -quinol when kept, the calorimetric measurements were made on fresh samples. Frequent density checks were made on portions of the sample both before and after measurement, since  $\alpha$ - and  $\beta$ -quinol can be distinguished readily by determining their densities (1.33 for  $\alpha$ -, 1.26 for  $\beta$ -) by flotation. However, the pure samples of  $\beta$ -quinol appear to be much more stable than those obtained from ethyl alcohol.

*Results.*—Five different samples of  $\beta$ -quinol were used; the first three were prepared from ethyl alcohol, and the other two from *n*-propyl alcohol. The former samples retained appreci-

able amounts of solvent, and the values obtained are therefore too high. A correction can be made for this, and the corrected values are given in the last column of the table. The correction can only be approximate, however, as the actual state of the retained alcohol is uncertain.

*Heat of transformation of  $\alpha$ - into  $\beta$ -quinol.*

Sample	Purity, %, by titration	$\Delta H$ , kcal./mole	$\Delta H$ , corr. for retained alcohol	Sample	Purity, %, by titration	$\Delta H$ , kcal./mole
A	—	0.21 <sub>0</sub>	—	Samples from <i>n</i> -propyl alcohol :		
B	99.1	0.22 <sub>9</sub>	0.13	D	99.8	0.13 <sub>9</sub>
B	99.1	0.23 <sub>8</sub>		E	99.8	0.12 <sub>8</sub>
C	99.3	0.19 <sub>6</sub>	0.12	E	99.8	0.11 <sub>6</sub>
Average corrected value 0.12 <sub>5</sub>				Average value of $\Delta H = 0.13$ kcal./mole $= 0.5_4$ abs. kjoule/mole		

(The heat of solution of  $\alpha$ -quinol at these concentrations is 4.7 kcal./mole.)

The trace of impurity still remaining in the  $\beta$ -quinol in samples D and E will probably cause the values obtained to be too high, whilst small amounts of  $\alpha$ -quinol, if present, will act in the opposite direction. These effects are unlikely to be greater than 0.02 kcal., and hence we may write  $\alpha$ -quino (solid) =  $\beta$ -quinol (solid):  $\Delta H = 0.13 \pm 0.03$  kcal./mole =  $0.5_4 \pm 0.1_2$  abs. kjoule/mole.

*Discussion.*—Since  $\beta$ -quinol is less stable thermochemically than  $\alpha$ -quinol, the latter will be the stable modification at low temperatures if the two forms are enantiotropic (Robertson and Ubbelohde, *Proc. Roy. Soc.*, 1938, *A*, **167**, 122). However,  $\alpha$ -quinol also seems to be stable up to its m. p., since samples of  $\beta$ -quinol go over rapidly into  $\alpha$ -quinol at high temperatures, and hence the system  $\alpha$ - $\beta$ -quinol is probably monotropic.

The very small energy difference between the two forms of quinol may be explained by the more extensive hydrogen bonding in the  $\beta$ -form, which almost compensates for the energy lost by the fewer van der Waals contacts. A rather similar situation is found in the system  $\alpha$ - $\beta$ -resorcinol (Robertson and Ubbelohde, *loc. cit.*).

[*Added in proof*, 8.9.52.] Since this paper was submitted, an abstract has appeared of work by Nitta, Séki, Chihara, and Suzuki on the vapour pressures of crystalline intermolecular compounds (*Chem. Abs.*, 1952, **46**, 3820; *Sci. Papers Osaka Univ.*, No. 29), and further details have been kindly sent to us by Professor Séki. From vapour-pressure measurements on samples of quinol, these workers deduce a value for  $\Delta H_{\alpha-\beta\text{-quinol}}$  of  $-1.58 \pm 0.30$  kcal./mole, in marked disagreement with our value of  $+0.13 \pm 0.03$  kcal./mole. Nitta *et al.* claim to have prepared  $\beta$ -quinol by heating the methyl alcohol clathrate compound at 60° for about half a day in a high vacuum, but no analysis of the sample was made. We have attempted to repeat this preparation by heating some methyl alcohol clathrate compound at 60° for 20 hours under a "black" vacuum. On titration with ceric sulphate solution, the original sample contained 91.7% of quinol, corresponding to  $3C_6H_4(OH)_2 \cdot 0.93MeOH$ , and the product after heat treatment contained 93.2% of quinol. This indicates that only about 0.2 mol. of the original methyl alcohol had been removed. Flotation experiments also indicate the absence of appreciable amounts of  $\beta$ -quinol. The X-ray powder photographs of the methyl alcohol clathrate compound would, of course, be similar to that of  $\beta$ -quinol.

It seems likely therefore, that Nitta *et al.* were not working with pure samples of  $\beta$ -quinol

We are grateful to Mr. H. M. Powell for taking X-ray powder photographs of the samples of  $\beta$ -quinol. One of us (D. F. E.) is also indebted to the Department of Scientific and Industrial Research for a maintenance grant.