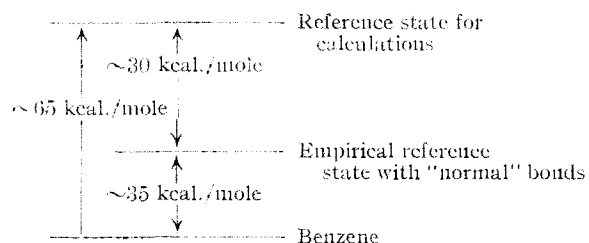


higher in energy than the empirical reference state containing normal single and double bonds. The magnitude of this difference may be estimated since it is obtained by stretching the double bonds and compressing the single bonds of a "normal" structure by 0.05 and 0.15 Å., respectively. If the normal single and double bond force constants are approximately  $5.0 \times 10^6$  and  $9.6 \times 10^5$  dynes/cm., we might guess that the energy difference between the reference states is of the order of 30 kcal./mole so that calculated resonance energies should be greater than empirical resonance energies by about this amount. This relation between the two reference states and the real molecule may be shown schematically as



A value of about 65 kcal./mole for the resonance energy calculated from the reference state with equal bond lengths reduces the discrepancy encountered in crude quantum mechanical calculations. In a zero order molecular orbital calculation the resonance energy and the energy of the first excited state are calculated in terms of one parameter. If the spectroscopic value for the energy of the first excited state is used to determine this parameter a resonance energy of 109 kcal./mole is obtained.<sup>12</sup> Ketelaar's first order treatment reduces this figure to 56 kcal./mole and his second order treatment cuts it to 40 kcal./mole. By comparison with the results obtained here, Ketelaar's final figure is definitely low.

In summary, it appears that (1) normal bond lengths in benzene are not sufficient to ensure normal structures and (2) that the empirical resonance energy of about 35 kcal./mole corresponds to a value of about 65 kcal./mole in the usual quantum mechanical calculation.

(12) This and the succeeding figures are taken from the table in ref. 11 by fitting the first electronic transition instead of the resonance energy.

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RECEIVED MAY 22, 1950

### The Isolation of Mandelic Acid from Cedar Tar

BY CARROLL L. KEY AND ROY T. CLARK, JR.<sup>1</sup>

The cedar tar, which was used in this investigation, was the residue obtained from the fractional distillation of the oil from the wood of *Juniperus mexicana*. A crude oil was obtained from this tar

(1) Abstracted from the thesis of Roy T. Clark, Jr., submitted in partial fulfillment of the requirement for the M. A. degree at the Southwest Texas State Teachers College, San Marcos, Texas.

by pyrolysis in an Engler distillation apparatus. The initial thermocouple reading inside the distillation flask during this process was 296° and the final reading was 380°. A 450-ml. fraction of oil which had a refractive index of 1.5014 at 25° and a boiling point range of 233–235° was obtained from the crude oil by fractionation in a vacuum fractionating still and systematic recombination of the cuts by refractive index and boiling point range through seven distillations. Several other fractions, which were obtained in this manner, were also investigated, but no mandelic acid was found.

#### Experimental

The saponification equivalent of the fraction of oil obtained by the above method indicated the presence of an ester which was probably the source of mandelic acid. This acid was isolated by refluxing the oil in 10% sodium hydroxide for three hours, acidifying the water layer, and extracting it with ethyl ether. The impure solid which remained when the ether evaporated was recrystallized from benzene. The melting point of this solid was found to be 118°; its molecular weight was 148 when determined by the Rast method; and its neutral equivalent was 153. The melting point was unchanged when a mixed melt of the unknown and pure DL-mandelic acid was made. The melting point of the anilide of the isolated acid was 152°, and the *p*-nitrobenzyl derivative melted at 124°. The foregoing data correspond to those listed for DL-mandelic acid.

**Yield.**—The total weight of the tar residue used to obtain the oil for this investigation was approximately 80,000 g., and the total weight of DL-mandelic acid recovered was approximately 4.5 g.; therefore, the yield of acid was less than 0.0001 of 1%.

DEPARTMENT OF CHEMISTRY

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### Heat Capacity of the Hydrazine–Water System<sup>1</sup>

BY E. W. HOUGH,<sup>2</sup> D. M. MASON AND B. H. SAGE

The isobaric heat capacities of hydrazine–water mixtures in the liquid phase at compositions from 0.5 to 1.0 weight fraction hydrazine were determined at bubble-point pressure in a stainless steel bomb calorimeter. Four sets of heat capacity measurements at different compositions were made in the temperature range from 40 to 90°. The density of the mixtures was determined for atmospheric pressure at 0 and 50°.

#### Experimental

A description of the equipment and techniques employed is available.<sup>3,4,5</sup> A stainless steel bomb calorimeter with a volume of approximately 1 liter was suspended by small wires within a vacuum jacket. An electrical heater was used to raise the temperature of the calorimeter and con-

(1) This paper presents the results of one phase of research carried out for the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. W-04-200-ORD-1482 sponsored by the U. S. Army Ordnance Department.

(2) Stanolind Oil and Gas Company, Tulsa, Oklahoma.

(3) B. H. Sage and E. W. Hough, *Anal. Chem.*, **22**, 1304 (1950).

(4) W. P. White, "The Modern Calorimeter," (The Chemical Catalog Co.) Reinhold Publishing Corp., New York, N. Y., 1928.

(5) N. S. Osborne, H. F. Stinson and E. F. Flock, *Nat. Bur. Standards, J. Res.*, **5**, 411 (1930).

tents which was established within 0.003° by means of a platinum resistance thermometer. The liquid sample within the calorimeter was agitated by a small centrifugal impeller. The energy measurements were made in watt-seconds and were converted to mean gram calories by the relation

$$1 \text{ thermochemical calorie} = 4.1840 \text{ abs. joules}$$

The apparatus was calibrated by measurements with water for which accurate thermodynamic data are available. The volume of the gas phase was maintained at less than 2.5% of the total volume of the calorimeter, and therefore simplifying assumptions in the calculations of the heat capacity from the thermal data are justified at temperatures below 100°.<sup>3</sup>

The hydrazine-water mixtures were prepared by diluting nearly pure hydrazine with distilled water and by refluxing the mixture at low pressures to remove dissolved gases. The compositions of the mixtures were determined from the quantity and composition of the hydrazine used and the weight of water added. It was found as a result of careful chemical analyses that the hydrazine contained less than 0.001 mole fraction of impurities. Analyses of the mixtures were also made and good agreement with the compositions computed from the gravimetric data was realized. Limited decomposition of the mixtures rich in hydrazine was evidenced at higher temperatures during the heat capacity measurements.

### Results

Smoothed values of the isobaric heat capacity of the hydrazine-water system at bubble point are shown in Table I for compositions from 0.5 to 1.0 weight fraction hydrazine in the temperature range from 40 to 90°. The maximum error of the

TABLE I  
SMOOTHED VALUES OF ISOBARIC HEAT CAPACITIES OF  
HYDRAZINE-WATER SYSTEM AT BUBBLE POINT

Com- position wt. fract. hydrazine	Isobaric heat capacity, cal./g., °C.					
	40°	50°	60°	70°	80°	90°
0.50	0.8511 <sup>a</sup>	0.8605 <sup>a</sup>	0.8761	0.8943	0.9126	0.9306 <sup>a</sup>
.60	.8351 <sup>a</sup>	.8430 <sup>a</sup>	.8546	.8673	.8783	.8887 <sup>a</sup>
.70	.8152 <sup>a</sup>	.8230 <sup>a</sup>	.8313	.8404	.8483	.8554 <sup>a</sup>
.80	.7902	.7985	.8057	.8134	.8203	.8258 <sup>a</sup>
.90	.7632	.7721	.7796	.7864	.7927	.7987 <sup>a</sup>
1.00	.7368	.7443	.7517	.7593	.7665	.7742 <sup>a</sup>

<sup>a</sup> These values are extrapolated.

heat capacity data is estimated to be 1%, and 75% of the values recorded in Table I probably do not involve uncertainties greater than 0.5%. In Fig. 1 is presented the heat capacity of pure hydrazine as a function of temperature and, for comparison, data reported in the literature<sup>6</sup> for this compound are also included. The smoothed heat capacity

TABLE II  
DENSITIES OF HYDRAZINE-WATER MIXTURES

Composition, wt. fract. hydrazine	Density	
	0°	50°
0.50	1.0078	1.0050
.60	1.0074	1.0046
.70	1.0063	1.0030
.80	1.0014	0.9976
.90	0.9925	.9893
1.00	.9816	.9780

(6) D. W. Scott, *et al.*, *THIS JOURNAL*, **71**, 2293 (1949).

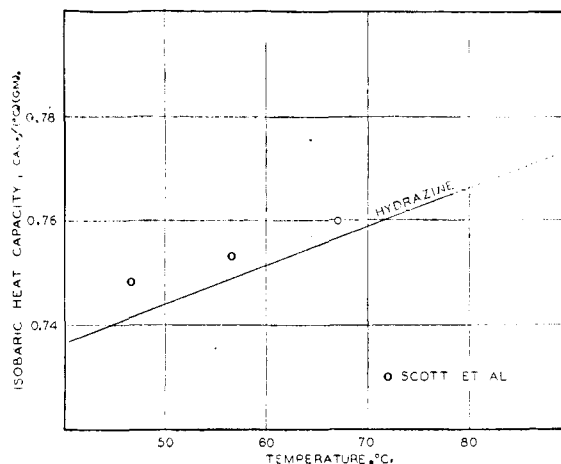


Fig. 1.—Isobaric heat capacity of hydrazine at bubble-point pressure.

data for the hydrazine-water system are depicted in Fig. 2. Density measurements were made with

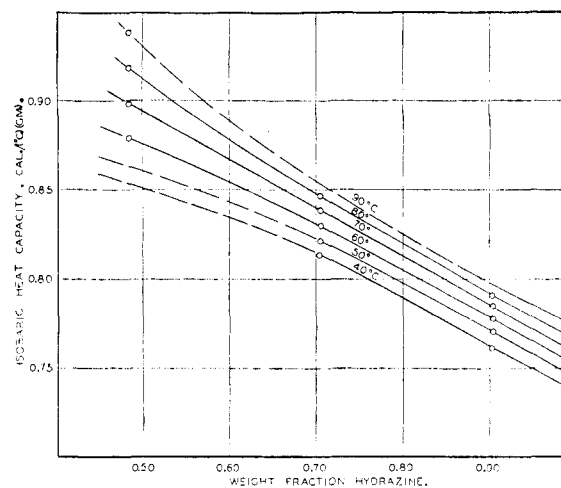


Fig. 2.—Isobaric heat capacity of the hydrazine-water system.

a pycnometer for a number of mixtures at compositions between 0.5 and 1.0 weight fraction hydrazine at temperatures between 0 and 50°. The smoothed data are presented in Table II and it is unlikely that they involve uncertainties larger than 0.1%.

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### Heat Capacities of Several Organic Liquids<sup>1</sup>

By E. W. HOUGH,<sup>2</sup> D. M. MASON AND B. H. SAGE

The isobaric heat capacities of aniline, ethylenediamine, furfuryl alcohol, isopropylamine, methyl

(1) This paper presents the results of one phase of research carried out for the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. W-04-200-ORD-1482 sponsored by the U. S. Army Ordnance Department.

(2) Stanolind Oil and Gas Company, Tulsa, Oklahoma.