The positive excess entropies of mixing shown by mixtures of ethylene bromide with chlorobenzene and 1-nitropropane confirm very nicely our previous free energy measurements on these mixtures. The present free energy measurements on mixtures of chlorobenzene–1-nitropropane suggest only slightly that the excess entropy is negative; the heats of mixing prove definitely that this is so.

In our previous communication, we pointed out that there was no simple relation between the excess free energy and entropy of mixing, but that the percentage volume change and the entropy change always possessed the same sign. Mixtures of chlorobenzene–1-nitropropane conform to this rule as both quantities are negative. In Fig. 2 we have graphed the percentage volume change against TS^E for the present mixtures and for the three possible binary systems from carbon tetrachloride, benzene and cyclohexane studied by Scatchard and co-workers.[6] A fairly good straight line passing through the origin is obtained. Mixtures of chloroform and ethanol[9] satisfy the above rule, but a very small volume change is accompanied by a relatively large entropy change. As far as the present comparison is concerned, the latter mixture is abnormal.

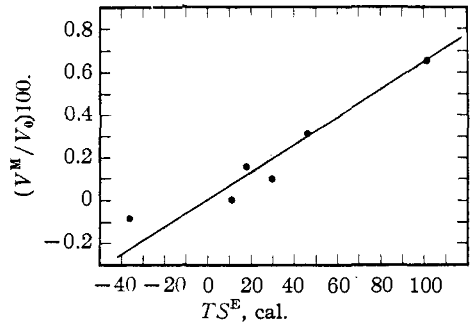

Fig. 2.—Percentage volume change *versus* TS^E at 30° for the possible binary mixtures from CCl_4, C_6H_6, C_6H_{12} and from C_6H_5Cl, $C_2H_4Br_2$, $C_3H_7NO_2$. Mole fraction is 0.5.

Summary

The excess free energy of mixing for the system chlorobenzene–1-nitropropane has been measured at 75 and 120°. The heats of mixing of the three possible binary systems from ethylene bromide, chlorobenzene and 1-nitropropane have been determined for approximately equimolar mixtures. The data now on hand indicate that the excess entropy of mixing is approximately a linear function of the per cent. volume change for a considerable variety of liquid mixtures.

PROVIDENCE, R. I. RECEIVED JUNE 5, 1941

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(9) G. Scatchard and C. L. Raymond, THIS JOURNAL, **60**, 1278 (1938).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BRITISH COLUMBIA]

The Densities and Surface Tensions of *cis*- and *trans*-Decahydronaphthalene between −30 and 180°[1]

BY W. F. SEYER AND CHARLES H. DAVENPORT

This is the second of a series of papers dealing with the physical-chemical properties of the *cis* and *trans* isomers of decahydronaphthalene. The method employed in obtaining these compounds in a high state of purity has been described already in a previous article.[2] In view of Wightman's deductions from specially constructed spatial models that the *cis* and *trans* forms might be only the limiting stable forms of a series of unstable ones, it became of interest to investigate the variation of certain of their physical properties with temperature.[3] The properties selected for the work, described below, were the densities and surface tensions of the hydrocarbons between −30 and 180°.

Materials.—The materials were part of the lots already described which had the freezing points −43.26 and −31.47° for the *cis* and *trans* forms, respectively.

Procedure.—The density was measured by finding the loss in weight of a quartz sinker, when immersed in the liquid hydrocarbon. From its weight in air, 31.0059 g., and in water 22.5162 g., its volume at 20° was calculated to be 8.5150 cc., after all corrections for buoyancy had been made. The sinker was suspended from the bottom of a balance pan by means of a fine platinum wire which had been platinized over the region where the wire came in contact with the surface of the liquid in order to minimize the surface tension forces. Much care was taken to see that the sinker was always immersed to the same depth before taking a weighing and by using the figure 0.000038 for the coefficient of cubical expansion of quartz it was

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(1) Original manuscript received July 12, 1939.

(2) Seyer, THIS JOURNAL, **60**, 2125 (1938).

(3) W. A. Wightman, *J. Chem. Soc.*, **127**, 1421 (1925).

possible to correct its change in volume for each temperature. All these weighings were corrected to vacuum. The temperatures were measured by a Leeds and Northrup platinum resistance thermometer with a quartz stem. It had recently been calibrated for accuracy by the U. S. Bureau of Standards and its constancy was checked from time to time with melting ice.

Surface Tension.—Determinations of surface tensions were made according to the method suggested by Richards, Speyer and Carver.[4] The radii of the tubes were 0.033 and 0.121 cm. The constant K for the apparatus was found by measuring the difference in liquid level when partially filled with purified benzene. The average value of K over the region employed was found to be 23.63 with a deviation from the mean of 0.01. Both the glass tube and the capillaries themselves were examined for optical imperfections. To discover whether any errors were introduced by reading the difference of level through the wall of the bath which was made of Pyrex glass, the difference in level was first read with the surface tension apparatus in air; it was next read through the wall of the container filled with methyl alcohol, then filled with water and finally, with petrolatum oil, all at room temperatures. No difference in the readings could be detected by the cathetometer used which could be read to 0.002 cm. This instrument had also been calibrated against a standard meter scale. To ensure still further against the introduction of optical errors, differences in level were read both when the surface tension apparatus was immersed in methyl alcohol and then in water-baths at 10 and 20°, similarly for water and petrolatum oil at 60 and 70°, but the same results were obtained each time at the same temperature within the limits of experimental error.

The complete apparatus was so set up that all measurements could be made at the same temperature. The temperature could be held constant to within 0.03° by means of a thermoregulator and two heaters, the one being a sheathed Cenco knife, and the other just a bare nichrome wire. The thermoregulator was connected to the latter because this gave very little lag. The current passing through the sheathed heater was set for a definite value for each temperature and acted thus as an auxiliary source of heat.

Below 0° the temperature of the bath was controlled by allowing a stream of methyl alcohol, cooled to a definite temperature by being in contact with dry-ice, to run in near the stirrer.

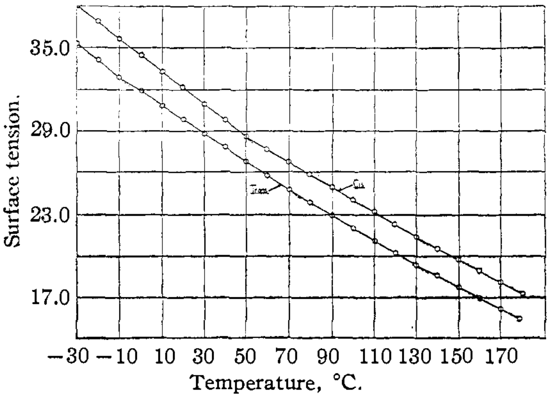

Fig. 1.—Surface tension of *cis*- and *trans*-decalin.

The time required for a complete series of readings was from two to three hours. The constant temperature desired was always approached in such a manner as to give a falling meniscus in the surface tension tubes. Usually no difference in level could be discerned about one-half hour after the temperature remained constant.

The densities in g. per cc. (corrected to vacuum) and the surface tensions in dynes per cm. are given for the various temperatures in Table I.

TABLE I

Temp., °C.	Density, g. per cc. *cis*	Density, g. per cc. *trans*	Surface tension, dynes per cm. *cis*	Surface tension, dynes per cm. *trans*
−30	0.9350	0.9072	38.02	35.29
−20	.9274	.8997	36.83	34.14
−10	.9196	.8922	35.65	32.95
0	.9120	.8849	34.50	31.91
10	.9044	.8775	33.36	30.87
20	.8967	.8700	32.18	29.89
30	.8892	.8627	31.01	28.87
40	.8817	.8553	29.81	27.81
50	.8742	.8480	28.63	26.77
60	.8667	.8405	27.67	25.82
70	.8592	.8331	26.82	24.82
80	.8519	.8255	25.88	23.95
90	.8442	.8178	24.95	23.02
100	.8368	.8104	24.04	22.02
110	.8294	.8025	23.14	21.05
120	.8218	.7952	22.25	20.22
130	.8144	.7876	21.38	19.39
140	.8066	.7798	20.56	18.65
150	.7986	.7717	19.76	17.85
160	.7906	.7638	18.89	16.98
170	.7825	.7555	18.04	16.17
180	.7745	.7474	17.18	15.44

Discussion of Results

The results were plotted on a large scale graph (1 × 1.5 ms.). From this it was found that the density–temperature curves for both forms were very nearly linear and practically parallel over the entire temperature range measured. The formula given in the "International Critical Tables,"[5] when applied to the figures, gave a calculated density value for the *cis* differing from the found by less than 0.08% over the temperature range of −30 to 160°, and for the *trans* 0.05%. The value of the constants, α, β, γ in the equation

$$d_t = d_s + 10^{-3}\alpha(t - t_s) + 10^{-6}\beta(t - t_s)^2 + 10^{-9}\gamma)t - t_s)^3$$

are given in Table II.

TABLE II

Maximum	deviation	ds	α	β	γ
cis	0.0007	0.9120	−0.76092	+0.00919	−0.00278
trans	0.0004	0.8849	−0.07396	−0.00342	−0.01655

The values for the densities of the two hydrocar-

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[4] Richards, Speyer and Carver, THIS JOURNAL, **46**, 1196 (1924).

[5] "International Critical Tables," Vol. III, p. 27.

bons given previously were the mean of four determinations when using a specific gravity bottle. The present values differ from the former by 7 units in the fourth place for the *cis* and 1 unit for the *trans*. The present values are regarded as the more accurate of the two.

The surface tension data were plotted on the same large scale graph mentioned above (Fig. 1). The curves obtained were not quite straight lines. The regions of pronounced deviations from linearity have been indicated in Fig. 1 by the broken lines. These deviations may be due to errors as it was noticed that in certain regions it was much more difficult to check results than in others.

There appears to be a considerable change in slope for the *cis* compound at 50°. In this region it was possible to check the differential height readings to within 0.01 cm. of the two samples that were tested. Both samples were measured repeatedly at 60 and 70°, then cooled and measured at 20, 30, 40 and 50° in order to determine whether some change in the *cis* form did take place. Since it is felt the results are accurate to within 1% over the temperature range from 20 to 70°, some significance must be ascribed to the change in slope of the temperature–surface tension curve at 50°. Just what the nature of the change is cannot be explained at present. However, other measurements now in progress indicate that the *cis* form behaves in an abnormal manner in the temperature region about 50°.

Summary

1. The densities and surface tensions of *cis*- and *trans*-decahydronaphthalene have been measured from −30 to 180°.

2. The density–temperature relations are nearly linear, but the others deviate somewhat from linearity.

VANCOUVER, B. C. RECEIVED JUNE 3, 1941

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Rates of Ammonolysis of Some α-Halogen Acids and α-Halogen Acyl Peptides[1]

BY ALBERT F. CHADWICK[2] AND EUGENE PACSU

The most important method used for the synthesis of polypeptides is that which consists of first condensing an α-halogen acyl halide with an α-amino acid or with a di-, tri-, etc., peptide and then treating the condensation product with ammonia. This gives a polypeptide containing one more amino acid residue than the starting compound. Many amino acids themselves are synthesized from α-halogen acids and ammonia. Up to the present time the ammonolysis step in the synthesis has not given satisfactory yields as a rule. This is partly due to the hydrolysis which takes place if the polypeptide product is left longer in the concentrated ammonia solution than is necessary and partly due to the reaction between some of the amino compound as it is formed and the unreacted halogen compound, resulting in substituted secondary and tertiary amines.[3]

Emil Fischer, who has done the most work in this field, experimented with varying his reaction conditions but still selected them arbitrarily and made no quantitative study. He prepared diglycylglycine from chloroacetylglycylglycine by treating the latter compound with 25% aqueous ammonia for fifteen hours at room temperature.[4a] In the same paper, however, he describes the preparation of triglycyl- and tetraglycylglycine by boiling the corresponding chloroacetyl derivatives with concentrated ammonia for an hour. The same conditions were used in the preparation of leucylalanine from α-bromoisocaproylalanine,[4b] while leucylglycylglycine was prepared[4a] by boiling α-bromoisocaproylglycylglycine with ammonia for only half an hour. When several years later Abderhalden and Fodor[5] prepared diglycylglycine, they used more drastic conditions than did Fischer, treating the chloroacetyl compound with 25% ammonia for twenty-four hours at 37°. Their yield was no better than Fischer's. More recently, however, Abderhalden and co-workers[6] have made some quantitative measurements on

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[1] This work was supported in part by a grant from the Rockefeller Foundation.

[2] Ethyl Gasoline Corporation Fellow in Chemistry.

[3] (a) Robertson, THIS JOURNAL, **49**, 2889 (1927); (b) Cheronis and Spitzmueller, *J. Org. Chem.*, **6**, 349 (1941).

[4] (a) Fischer, *Ber.*, **37**, 2486 (1904); (b) Fischer, *Ann.*, **340**, 123 (1905).

[5] Abderhalden and Fodor, *Ber.*, **49**, 561 (1916).

[6] (a) Abderhalden and Heumann, *Z. physiol. Chem.*, **205**, 271 (1932); (b) Abderhalden and Beckmann, *ibid.*, **207**, 93 (1932); (c) Abderhalden and Bahn, *Ber.*, **63**, 914 (1930).