The authors desire to express their thanks to Professor Charles H. Skinner of the Department of Physics, Ohio Wesleyan University, for the potentiometer used in this investigation.

Summary

1. A new determination of the transference numbers of the ions of hydrochloric acid has been made.

2. It has been shown that the addition of gelatin reduces the effective hydrogen-ion concentration of 0.1 M and 0.01 M hydrochloric acid solutions.

3. The transference numbers of 0.1 M and 0.01 M hydrochloric acid have been found to be changed by the presence of gelatin.

4. The presence of gelatin alters the conductivity of 0.1 M and 0.01 M solutions of hydrochloric acid.

5. *Some evidence has been found which apparently substantiates the* theory that gelatin reacts with acids to form an adsorption complex or additive chemical compound which dissociates. This is in agreement with the views set forth by Jacques Loeb.[10]

COLUMBUS, OHIO

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

A CALORIMETER FOR HEATS OF MIXING AT ELEVATED TEMPERATURES[1]

BY BURT H. CARROLL AND J. HOWARD MATHEWS

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In the numerous investigations of the properties of liquid mixtures, heat of mixing has received comparatively little attention. Quantitative theoretical treatment has been thus far unsuccessful; the attempt of Kremann[2] to compute heat of formation of a mixture from the constants of the van der Waals equation for the components was not verified by experiment. It is improbable that such calculations can be made until our knowledge of the liquid state is more complete and accurate. However, the work of van der Waals has indicated clearly that heat effects are to be expected, independent of molecular change, when the mixture is nonideal. In some cases heat of mixing may be definitely, if not quantitatively, ascribed to polarity. A considerable liberation of heat, accompanied by a minimum vapor pressure, is strong evidence for the formation of a

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[10] Loeb, "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Co., **1922**.

[1] This paper constitutes a portion of a thesis presented by Burt H. Carroll to the Graduate School of the University of Wisconsin, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in June, 1922.

[2] Kremann, *Monatsh.*, **35**, 1235 (1914); **37**, 11 (1916).

compound; conversely, absorption of heat and maximum vapor pressure constitute evidence that one or both of the liquids, associated in the pure state, have decreased in association on dilution.

In the course of an investigation of mixed solvents,[3] it became necessary to calculate the heat of vaporization of several binary mixtures at 760-mm. pressure. This necessitated a knowledge of the heat of mixing at the boiling point. No data being available, it was necessary to design and construct a calorimeter for the purpose. Although the accuracy required was not greater than 0.1 calorie per gram, the mechanical features of the apparatus presented some difficulties, as the pressure before mixing was over two atmospheres in some cases.

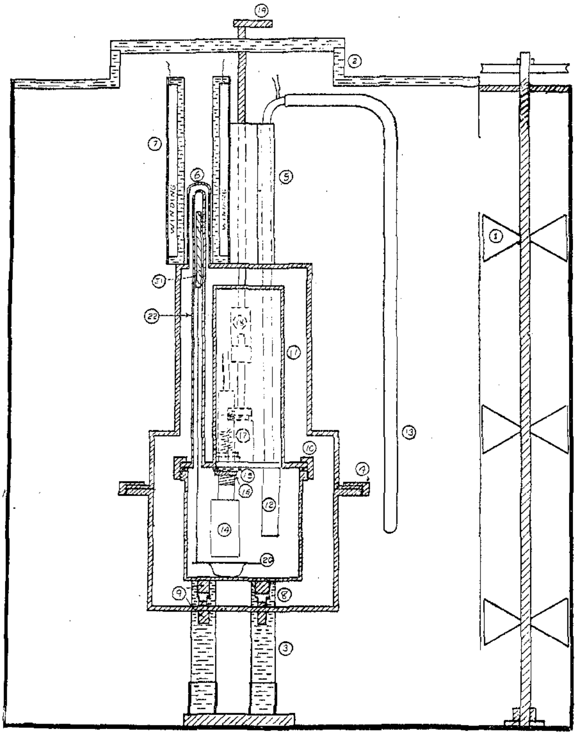

Fig. 1

The apparatus is shown in section in Figs. 1 and 2. As the liquids were inert in character, the calorimeter was made from seamless brass tubing. The body was 5.4 cm. in diameter and depth; a heavy threaded ring soldered around the top provided a good bearing surface for the cover, and engaged the locking ring (10) in the diagram. The joint was made tight by a ring of steam packing; for organic liquids the composition of graphite and

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[3] To be published later.

paper pulp known under the trade name of "Permanite" was very satisfactory.

One of the liquids was weighed into the body of the calorimeter; the other was sealed into an elongated, thin glass bulb, which was placed in the cylindrical extension of the cover (11). The liquids were mixed by breaking the projecting end of the bulb. The coil spring (25) and trigger (24) for this purpose are shown in the horizontal section. The trigger was threaded to a brass rod, passing out through the stuffing box (17), and thermally insulated by the socket joint (18) of vulcanized fiber.

The stirrer was necessarily of the electromagnetic type. A tube (22), 3 mm. in internal diameter, extended up from the cover for 12.7 cm., into a slightly larger tube (6) on the "submarine" can. The soft iron armature (21) of the stirrer was thus brought into the solenoid (7). The stirrer proper, a piece of thin sheet aluminum, was connected to the armature by aluminum wire. The stroke was about 9 mm., 20 times a minute; current in the solenoid was interrupted by a commutator belted to the main stirrer. The heat generated in the solenoid was carried off by the adiabatic bath, which surrounded it; the solenoid was not in thermal contact with the tube (6).

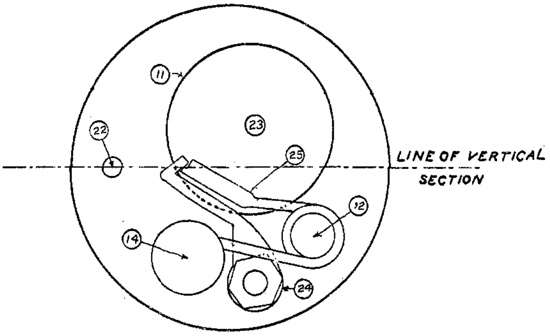

Fig. 2

The pressure changes on mixing would have made impossible the use of a mercurial thermometer in the calorimeter, even if there had not been the mechanical difficulty of making a tight joint around the stem. The procedure adopted was to place the thermometer in the outer bath, and use a sensitive differential thermel with its ends in the bath and calorimeter, respectively. The calorimeter was operated adiabatically, using the couple as a null instrument; all actual readings of the temperature were accordingly made on the mercury thermometer in the outer bath. The thermel consisted of a 4-junction copper-constantan element, used with a low resistance galvanometer, whose sensitivity was 0.0067° per centimeter on the scale.

As the heat capacity of the liquids varied widely, the total heat capacity was determined electrically for each experiment. The heater (14) was of fine manganin wire, insulated with mica, and was inclosed in a very thin cylindrical copper sheath. Its resistance was 29.3 ohms at room temperature. It was thermally insulated from the calorimeter. The tube carrying the lead wires was of heavy brass, threaded, and somewhat smaller than the hole through the cover. Redmanol washers (15) were clamped down on each side of the cover by nuts (16) on the tube. The joint was painted with Redmanol varnish and baked; it was mechanically strong and perfectly tight. The heavy copper lead wires passed out through the adiabatic bath in oil-filled U-tubes, to prevent thermal leakage. The electrical energy was measured by a calibrated ammeter and voltmeter; the latter was a large commercial laboratory instrument, taking negligible current (resistance 13,000 ohms).

The "submarine" can was of heavy brass tubing, with a joint similar to that in the calorimeter. The air gap was 13 mm., except where necessarily increased by the irregular shape of the calorimeter. The wires and rods from the calorimeter were led out through tubes on the top of the can, which was submerged 5 cm. below the level of the bath. It was supported in the bath by three 5cm. fiber rods.

The adiabatic bath was of heavy sheet copper, 23 cm. in diameter and 30.5cm. high, thus giving about 5 cm. of liquid all around the submarine can. The propeller stirrer revolved in a side tube connected to the main bath by openings at the top and bottom. The bath was filled with a very dilute solution of ferric chloride in a mixture of $^3/_4$ glycerol and $^1/_4$ water. It was heated electrolytically, as first described by Daniels,[4] using a current of 110 volts, 60 cycle a. c. One terminal was connected to the submarine can, the other to the bath. Current was regulated by slide-wire resistances; 40 ohms' range was necessary, as the resistance of the bath dropped from 25 ohms at 25° to 10 ohms at 80°. The electrolytic heating was very satisfactory; with little attention the bath could be kept constant to ± 0.01° at all temperatures between 30° and 85° in spite of frequent fluctuations in the voltage. The temperature could be raised from 1° to 3° per minute, depending on the temperature range; as the heat was generated in the bath itself, there was no lag. Corrosion with the alternating current is slight, but it was found advisable to protect soldered joints by a coating of Redmanol varnish. The bath was insulated thermally by asbestos packing placed between it and a larger vessel.

It was necessary to allow the system to stand at the desired temperature for a considerable time, to be certain that the liquid in the bulb had reached the temperature of the rest of the calorimeter. At the start of a determination, the bath and calorimeter were brought to the required temperature, using the heater to raise the temperature of the calorimeter at the same rate as that of the bath. The bath was then held at approximately

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[4] Daniels, THIS JOURNAL, **38**, 1473 (1916).

constant temperature for two or three hours, usually without attention. The fact that the calorimeter was filled with saturated vapor under pressure aided greatly in reaching thermal equilibrium quickly. Finally, the bath was held accurately constant until it was certain that the calorimeter temperature was not changing. Equilibrium was seldom reached with zero difference between calorimeter and bath; therefore, the same difference was maintained before and after mixing.

The liquids mixed very rapidly, with a correspondingly rapid change in temperature; and for this reason isothermal operation might have been more advisable. In cases where a rise in temperature was expected, energy was thrown into the bath as soon as the liquids were mixed; where heat was absorbed, current was shut off the bath and turned on the heater in the calorimeter, to minimize the total temperature change. All energy used in the calorimeter heater was of course measured. Equilibrium was reached quickly, the temperature becoming nearly constant in three or four minutes. After equilibrium was attained, the temperature was raised a carefully determined amount by the calorimeter heater, for the determination of heat capacity.

All determinations were made at the boiling point of the mixture in question. The possible heat effects due to evaporation or condensation on mixing were calculated from the known vapor pressures and the volume of the calorimeter; the correction was in all cases smaller than the experimental error.

TABLE I

HEAT OF FORMATION OF MIXTURES

The negative sign indicates absorption of heat

% of first component	Mole fraction	Temperature at mixing. °C.	Heat of mixing Cal. per g.	Heat of mixing Cal. per mole
		Ethyl alcohol-water		
28.8	0.157	79.2	+1.75	+ 38.0
59.0	.360	77.0	−0.66	− 18.7
		Benzene-ethyl alcohol		
28.8	.193	68.9	−3.72	−194
47.8	.351	68.5	−6.31	−360
70.0	.580	68.2	−3.57	−230
		Ether-acetone		
25.5	.211	46.3	−1.21	− 74.5
46.1	.406	40.5	−2.07	−133
51.9	.544	40.0	−1.45	− 96.5
71.8	.666	37.1	−1.65	−113
		Chloroform-acetone		
42.1	.262	57.0	+3.94	+290
53.5	.359	58.95	+4.69	+375
76.5	.614	62.05	+4.49	+369
		Carbon tetrachloride-ethyl acetate		
44.1	.308	74.8	−0.57	−62

Table II

Boiling Points of Mixtures

Mole fraction first component	Ethyl alcohol-water °C.	Benzene-ethyl alcohol °C.	Ether-acetone °C.	Chloroform-acetone °C.	Carbon tetrachloride-ethyl acetate °C.
1.0	78.3	79.4	34.5	61.09	76.88
0.9	78.2	71.5	35.0	63.45	76.00
.8	78.3	69.4	35.6	64.18	75.38
.7	78.4	68.3	36.5	64.30	75.05
.6	78.7	68.0	37.6	64.00	74.98
.5	79.3	68.0	39.0	63.25	75.02
.4	80.2	68.4	40.8	62.21	75.18
.3	81.2	69.2	43.4	60.93	75.44
.2	82.8	70.4	46.9	59.38	75.84
.1	86.2	73.1	51.4	57.62	76.56
.0	100.0	78.3	56.2	56.12	77.40

The liquids had been purified by suitable chemical treatment, followed by fractionation. The greatest source of error is, undoubtedly, the failure to maintain adiabatic conditions in the period immediately after mixing; it is for this reason that isothermal operation would be preferable. On plotting the apparent calorimeter temperature against time for a determination, irregularities are apparent which introduce an uncertainty of as much as ± 0.05° in the initial and final temperatures. The heat capacity of calorimeter and liquids being generally about 100 calories per degree, this corresponds to a possible maximum error of 10 calories in heat of formation of 60 to 110 g. of mixture. Check determinations unfortunately were not completed on mixtures of identical composition; the deviation of individual points from the smoothed curves indicates a probable error of 0.1 to 0.2 calorie per gram. This was sufficient accuracy for the purposes of the experiments, and limitations of time prevented alteration of the apparatus.

In two cases only is it possible to compare the data with those of other investigators. The results of Bose[5] for heat of mixing of ethyl alcohol and water at 74°, are represented in Fig. 3 on the same curve with the data obtained at the boiling point. (Crosses mark the points obtained by Bose.) Sameshima[6] quotes some unpublished results of H. Hirobe on heat of mixture of ether and acetone at 25°; the difference from the results obtained at the boiling point indicates that the heat effect increases with rise of temperature.

The marked positive heat effect in the case of mixtures of chloroform and acetone, reaching a maximum in the equimolecular mixture, may be considered evidence for the formation in solution of the compound, which may be isolated at lower temperatures. Similarly, the absorption of heat

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[5] Bose, *Göttinger Nachr. Math. Phys. Kl.*, **1906**, 277, 309, 335.

[6] Sameshima, This Journal, **40**, 1482 (1918).

on dilution of ethyl alcohol with benzene may be ascribed to decrease in the association of the alcohol. The heat effects in the other three cases do not offer conclusive evidence as to change in molecular state.

Thanks are due to Professor Farrington Daniels for assistance in the design of the calorimeter. This investigation was carried out under a DuPont Fellowship, and the generosity of the donor is gratefully acknowledged.

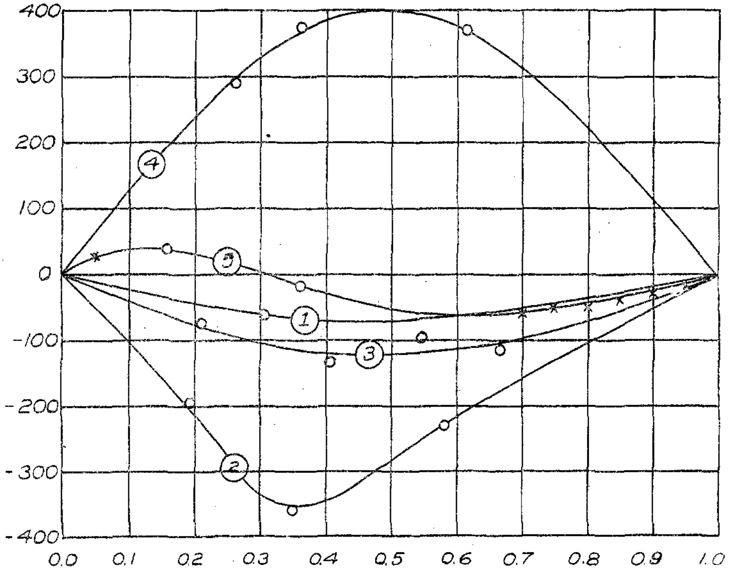

Fig. 3.—Heat of mixing, in calories per mole, plotted aginst mole fraction of the first component. (1) Carbon tetrachloride—ethyl acetate; (2) Benzene—ethyl alcohol; (3) Ether—acetone; (4) Chloroform—acetone; (5) Ethyl alcohol—water

Summary

1. A calorimeter has been designed and constructed, capable of measuring heats of mixing at temperatures up to the boiling point of the mixture.
2. Data are presented for heats of formation of five binary mixtures of various types.

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