weights of the constituents, *i. e.*, corresponds to a definite chemical formula. The cause of this, according to the theory derived by Denison, is the actual production of a compound, for he has shown theoretically that the maximum deviation of a physical property from the mixture law must occur at that point when a compound of the constituents is present to a maximum extent, *i. e.*, where the composition of the mixture leading to the maximum deviation is of the same composition as the compound formed.

The molecular compounds found to exist in liquids by the above work on the basis of this theory (in other words, the molecular (*chemical*) compositions found empirically here to lead to the maximum deviation of the *physical* property from the mixture law) are as follows (in a number of cases the other physical properties, viscosity and density, leading to the same result):
$(CH_3)_2CO.10H_2O$; $2(C_6H_5OH).(CH_3)_2CO$; $C_6H_5OH.2(C_2H_5OH)$; $C_6H_6.2(CH_3COOH)$; $2(C_6H_6).C_2H_5OH$; $C_6H_6.CH_3OH$ and $4(C_6H_5OH).3(C_6H_6)$.

5. The compound shown to exist in the system benzene–acetic acid, *viz.*, $C_6H_6.2(CH_3COOH)$, is most interesting when considered in the light of the results of other methods, which lead to the conclusion that acetic acid is always doubly polymerized in benzene solution. These methods are such, however, as would have failed to show a combination of the solvent with the polymerized solute, even if it did exist; and hence the evidence found here pointing to such a compound is not only not inconsistent, but gives a more advanced point of view on the process we have designated in the past as a simple polymerization.

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THE SPECIFIC HEATS AND HEATS OF FUSION OF TRIPHENYLMETHANE, ANTHRAQUINONE AND ANTHRACENE.[1]

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The following investigations were undertaken with the purpose of securing data to be used in the prediction of solubility according to the principles recently outlined by one of us.[2]

The calorimeter was similar to that described by G. N. Lewis and Merle Randall,[3] with the exception that the material was heated not in a vapor

[1] The data herein presented, with the exception of those pertaining to anthracene, are taken from the thesis presented by Alice D. Duschak in partial fulfillment of the requirement for the degree of Master of Arts.

[2] J. H. Hildebrand, THIS JOURNAL, 28, 1452 (1916).

[3] THIS JOURNAL, 33, 476 (1911).

bath, but in an aluminum cylinder 33 cm. high and 11 cm. in diameter, with a hole 2.5 cm. in diameter running through its axis. This cylinder was wound with nichrome wire and packed in asbestos in a box which allowed access to both the top and bottom of the central hole. By maintaining a constant current in the wire it was possible to secure a very constant temperature in the cylinder when the ends of the hole were closed. The high conductivity of aluminum for heat assured a uniform temperature throughout the central hole. This box was supported so that the half-liter Dewar tube which serves as a calorimeter vessel could be slid under it to receive the material heated within the aluminum cylinder.

The usual precautions in calorimetric work were observed, such as thorough and uniform stirring, protection from draughts, the calibration of the thermometers, etc. The heat capacity of the calorimeter was determined by using a cylinder of pure copper weighing 140.5 g., and heated to 100°. For the mean specific heat of copper between 20° and 100° the value determined by Schmitz[1] was used, 0.0936 cal. Since the heat capacity of the calorimeter vessel, stirrer, etc., was only about 10% of that of the water used, any error in the specific heat of copper would introduce one-tenth that error in our later values.

The triphenylmethane used was prepared from chloroform and benzene, using the Friedel and Crafts reaction. The resulting material was recrystallized twice from benzene and once from alcohol. The former being non-polar and the latter polar, this treatment would tend to remove impurities belonging to both classes. The melting point, determined with a calibrated thermometer, was found to be 92.3°, agreeing with values given in the literature.[2] The anthraquinone was purified by recrystallization from benzene and alcohol. Its melting point was 282.0°. Values given in texts on organic chemistry, mostly without original references, range from 273° to 285.9°. The higher figures are doubtless more nearly correct, as most impurities would tend to lower the melting point. The anthracene was a very pure preparation from a commercial source and was used without further preparation. The melting point of anthracene is taken as 216.55°.[3]

A container for the materials under investigation was required, and "pyrex" glass with its remarkably low coefficient of expansion was used for all but the work with anthraquinone at the highest temperature, where it was necessary to substitute quartz. The specific heats of these materials were therefore determined with the following results:

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[1] Schmitz, *Proc. Roy. Soc. London*, **72**, 177 (1903).

[2] *Beilstein*, III, 406 (293).

[3] Reissert, *Ber.*, **23**, 2245 (1890).

SPECIFIC HEAT OF PYREX GLASS.

Temp. range.	Weight glass.	Ht. capacity of calorimeter.	Temp. rise. in calorimeter.	Fall in temp. of glass.	Sp. ht. glass.	Mean.	Calculated.
20–100°	21.71	656.0	0.538	82.5	0.1970		
20–100°	21.71	656.0	0.507	78.8	0.1944		
20–100°	21.71	655.5	0.517	79.8	0.1955	0.1956	0.1956
20–135°	21.71	656.0	0.807	120.4	0.2025		
20–135°	21.71	655.5	0.799	119.2	0.2023		
20–135°	21.71	655.0	0.777	118.1	0.1986	0.2011	0.2019
20–200°	21.71	656.0	1.323	185.3	0.2157		
20–200°	21.71	655.5	1.305	184.9	0.2130		
20–200°	21.71	656.0	1.288	178.2	0.2184	0.2157	0.2136
20–265°	14.58	656.0	1.244	248.5	0.2252		
20–265°	14.58	655.5	1.243	248.0	0.2252		
20–265°	14.58	655.0	1.234	246.2	0.2251	0.2252	0.2254
				Quartz glass.			
20–320°	9.576	656.0	0.938	297.3	0.2162		
20–320°	9.576	656.0	0.936	296.7	0.2161	0.2161[1]	

The values given for pyrex glass in the last column are calculated on the basis of the formula $c_t = 0.174 + 0.00036t$, where c_t denotes the specific heat at the centigrade temperature t. The mean specific heat between two temperatures t_2 and t_1, as used in this and subsequent calculations, is then given by the expression $0.174 + 0.00018\ (t_2 + t_1)$. It will be noted that the calculated values agree very closely with the measured except for the interval 20–200°, where the experimental value is evidently too high. The poorer agreement between the individual measurements for this interval diminishes the weight that should be assigned to them.

Since we used quartz glass only in the temperature range 20–320°, the mean specific heat for this interval was all that was required.

The mean specific heats of solid triphenylmethane, anthraquinone and anthracene were determined between several temperature intervals, obtaining the values given in the following table:

Substance.	Temp. range.	Specific heat.				Mean.
Triphenylmethane	20–60°	0.2956	0.2995	0.2960	0.2961	0.2968
Triphenylmethane	20–85°	0.3288	0.3345	0.3293	0.3330	0.3314
Anthraquinone	20–132°	0.3068	0.3035	0.3033	0.3004	0.3037
Anthraquinone	20–200°	0.3322	0.3350	0.3357	......	0.3343
Anthraquinone	20–266°	0.3580	0.3583	0.3588	......	0.3584
Anthracene	20–100°	0.312	......	......	......	0.318
Anthracene	20–150°	0.340	......	......	......	0.340
Anthracene	20–210°	0.3603	0.3590	0.3610	0.3630	0.3608

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[1] From the measurements of Dieterici (*Ann. Phys.*, [4] **16**, 600 (1905)), Heinrichs (Inaug. Diss., Bonn, 1906) and Schultz (*Centr. Min. Geol.*, **1912**, 481) we calculate the following values for the mean specific heat of quartz glass: 0.2238, 0.2168 and 0.2126, respectively, the mean of the three being 0.2174.

The following expressions, calculated from the preceding figures, may be used to calculate the specific heats at various temperatures:

Triphenylmethane........ $c = 0.186 + 0.00277t$
Anthraquinone........... $c = 0.258 + 0.0007t$
Anthracene.............. $c = 0.280 + 0.0007t$

The expression for triphenylmethane is hardly trustworthy for extrapolation to lower temperatures, as the temperature range was so small. It would seem improbable that the temperature coefficient should be so large.

The heat of fusion and the specific heat of the liquid are determined simultaneously by measuring the total heat given up to the calorimeter by the fused material heated, first, slightly above its melting point, and, second, considerably above its melting point. This gives simultaneous equations whose solution gives the heat of fusion and the specific heat of the liquid. To form these equations the heat received by the calorimeter is equated to that given up by the cooling material, which is made up of four quantities, *i. e.*, that given up by the container, by the solid, by the liquid, and that evolved by the solidification of the latter. In the following calculations the mean specific heats of glass and solid substance in the corresponding temperature ranges were calculated by the expression $c_0 + a/2\ (t_1 + t_2)$, where the actual specific heat at the temperature t is given by the previous equations in the general form $c_t = c_0 + a\ t$.

In this way there were obtained pairs of equations for each of the three materials investigated, solution of which gave the values shown in the following tables:

Triphenylmethane.

Heat of fusion, l.	Specific heat of liquid, c.	From equations (temp. ranges, 20–100°; 20–135°).
17.85	0.480	$l + 7.2c = 21.30$
		$l + 44.4c = 39.16$
17.61	0.480	$l + 9.9c = 22.38$
		$l + 44.0c = 38.77$
18.00	0.477	$l + 8.8c = 22.20$
		$l + 43.8c = 38.90$
17.77	0.478	$l + 10.2c = 22.63$
		$l + 44.3c = 38.94$
17.80	0.479	

Anthraquinone.

Heat of fusion, l.	Specific heat of liquid, c.	From equations (temp. ranges, 20–290°; 20–320°).
37.8	0.690	$l + 10.1c = 44.8$
		$l + 38.5c = 64.4$
37.2	0.671	$l + 10.1c = 44.0$
		$l + 39.3c = 63.6$
37.3	0.615	$l + 10.1c = 43.5$
		$l + 39.4c = 61.5$
37.4	0.66	

Anthracene.

Heat of fusion, l.	Specific heat of liquid, c.	From equations (temp. ranges, 20–290°; 20–320°).
38.8	0.502	$l + 5.5c = 41.6$
		$l + 37.8c = 57.8$
38.6	0.515	$l + 4.9c = 41.1$
		$l + 38.1c = 58.2$

The corresponding values for the heats of fusion per mol of substance are as follows: triphenylmethane, 4340 cals.; anthraquinone, 7780 cals.; anthracene, 6890 cals.

Summary.

The following specific heats have been determined: pyrex glass, $0.174 + 0.00036t$; quartz glass, between 20° and 320°, 0.2161; triphenylmethane, solid $0.186 + 0.00277t$, liquid 0.479; anthraquinone, solid $0.258 + 0.0007t$, liquid 0.66; anthracene, solid $0.280 + 0.0007t$, liquid 0.509.

The following heats of fusion have been determined; triphenylmethane, 17.8 cals.; anthraquinone, 37.4 cals.; anthracene, 38.7 cals.

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SOLUBILITY AND INTERNAL PRESSURE.

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In a recent paper entitled "Solubility"[1] it was shown by the writer that deviations from Raoult's law, with accompanying effects upon the solubilities of gases, liquids and solids, appear to be governed by the internal pressures and polarities of the substances involved. Over one hundred instances were cited where the behavior of mixtures in this respect accorded with the theory. In the present paper is presented additional experimental evidence of the validity of this point of view.

Where Raoult's law is obeyed by the solution, the solubility of a solid at the absolute temperature T may be calculated by the aid of the equation

$$\log \mathrm{N} = \frac{-\mathrm{LTT}_m}{4.58\,(\mathrm{T}_m - \mathrm{T})},$$

where N is the solubility expressed in terms of mol-fraction, L is the molal heat of fusion, and T_m the melting temperature of the solute on the absolute scale. The difference between the specific heats of the solid and liquid forms of the solute is seldom known with sufficient accuracy to make it worth while to consider L as a function of the temperature.

Values of N so calculated for certain solids are given in Table I. Experimental values of the solubility are available mostly at 25°, hence N represents the solubility at that temperature, except for triphenylmethane

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[1] THIS JOURNAL, 38, 1452 (1916).