

as a proof of the correctness of the idea that dissolution of sodium is due to the reaction of the metal (electron) with the acid molecule.

5. The molal reactivity constant of various acids shows a tendency to increase with the strength of the acid. The effect of the charge of the acid and other effects, however, may partly mask the strength effect.

6. The roseo cobaltic ion which bears three positive charges reacts very rapidly with sodium amalgam. This is explained as being due to its high positive charge and the resulting strong attraction to the electron.

7. Corresponding to the high strength of the hydrogen ion H_3O^+ this acid reacts with extreme speed. The dissolution of sodium amalgam in strong acids is therefore governed chiefly by the rate of the diffusion process.

8. The rate of reaction of sodium amalgam with a solution of phenol in dry benzene is proportional to the phenol concentration.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, JOHNS HOPKINS UNIVERSITY]

THERMAL ENERGY STUDIES. I. PHENYL DERIVATIVES OF METHANE, ETHANE AND SOME RELATED COMPOUNDS¹

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The importance of energy as a factor in chemistry has been recognized for a great many years and it has been a source of inspiration in many fields of research from the time of Thomsen and Berthelot down to the present day. Broadly speaking, if we knew the energy relationships of the molecule completely enough, we would be able to predict all the modes of chemical behavior.

One must admit, however, that it is very difficult to do chemical thinking in terms of energy on the basis of our present knowledge. Although we intuitively connect chemical behavior with structural formulas or the position of an element in the periodic table, we have never been able to draw a sufficiently intimate picture of the relation of energy to molecular and atomic structure, so that we can feel instinctively the role of energy in determining the course of a reaction, particularly when it involves complex molecules. What we need is a much more detailed knowledge of the energy associated with the different parts of the molecule and how it varies with temperature, environment and distortion or excitation of the molecule itself.

For answering these questions, one of the most valuable types of information is heat capacity data especially over a wide range of temperature. During the past fifteen years there has been a great deal of work done in

¹ From the dissertation submitted by R. H. Smith in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

securing information along this line, especially by Gibson,² Latimer,² Parks,³ Giauque,⁴ Anderson⁵ and their associates, and by the group with which the present authors are connected.^{6,7} Especially within the last year this field of research has been greatly stimulated by developments in the interpretation of Raman spectra. It appears that the frequencies in these spectra correspond to the fundamental vibrations in the molecule, and that from them one can calculate the energy associated with individual parts of the molecule.^{8,9,10,11,12}

In view of this an investigation has been undertaken to study the thermal energy in a number of series of complex molecules for the purpose of learning more about energy distribution within the molecule and its variation with temperature and molecular structure. Preparatory to this project methods for heat capacity measurement have been developed especially designed to permit the survey of a large number of compounds within a reasonable length of time.⁶ A preliminary survey has also been made of the general considerations of energy distribution in complex molecules.^{7,12}

In the present series of papers it is planned to present the results of the experimental heat capacity measurements, followed by a discussion of the theory of the heat capacity of complex molecules and a comparison of the experimental values with values calculated from Raman spectra. This paper gives the data obtained from the phenyl derivatives of methane and ethane which were selected as the first group for the thermal energy study. It was felt that a knowledge of heat capacities would be particularly valu-

² Gibson, Latimer and Parks, *THIS JOURNAL*, **42**, 1533 (1920); Gibson, Parks and Latimer, *ibid.*, **42**, 1542 (1920); Gibson and Giauque, *ibid.*, **45**, 93 (1923); Latimer, *ibid.*, **44**, 90 (1922); Latimer and Hoenshel, *ibid.*, **48**, 19 (1926); Latimer and Ahlberg, *ibid.*, **52**, 549 (1930).

³ Parks, *ibid.*, **47**, 338 (1925); Parks and Kelley, *ibid.*, **47**, 2089 (1925); Parks and Anderson, *ibid.*, **48**, 1506 (1926); Parks and Huffman, *ibid.*, **48**, 2788 (1926); Parks, Kelley and Huffman, *ibid.*, **51**, 1969 (1929); Parks, Huffman and Thomas, *ibid.*, **52**, 1032 (1930); Huffman, Parks and Daniels, *ibid.*, **52**, 1549 (1930).

⁴ Giauque and Wiebe, *ibid.*, **50**, 101 (1928); **50**, 2193 (1928); **51**, 1441 (1929).

⁵ C. T. Anderson, *ibid.*, **52**, 2296, 2301, 2712, 2720 (1930).

⁶ Andrews, Lynn and Johnston, *ibid.*, **48**, 1274 (1926); Andrews, *ibid.*, **48**, 1287 (1926); Keesom and Andrews, *Verslag Konink. Akad. Wetens. Amsterdam*, **36**, 52 (1926); Andrews and Haworth, *THIS JOURNAL*, **50**, 2998 (1928); Andrews, *J. Franklin Inst.*, **206**, 285 (1928); Southard and Andrews, *ibid.*, **207**, 323 (1929); *ibid.*, **209**, 349 (1930).

⁷ Andrews, *Proc. Roy. Acad. Amsterdam*, **29**, 744 (1926); *Chemical Reviews*, **5**, 533 (1928); Bates and Andrews, *Proc. Nat. Acad. Sci.*, **14**, 124 (1928); Andrews and Southard, *Phys. Rev.*, **35**, 670 (1930).

⁸ Andrews, *ibid.*, **34**, 1626 (1929); **36**, 544 (1930).

⁹ Van Vleck, *Proc. Nat. Acad. Sci.*, **15**, 754 (1929).

¹⁰ Kettering, Shutts and Andrews, *Phys. Rev.*, **36**, 531 (1930).

¹¹ R. C. Yates, *ibid.*, **36**, 555, 563 (1930).

¹² A. B. Lewis, *ibid.*, **36**, 568 (1930).

able in a series such as this where, from the chemical standpoint, there appears to be a loosening of the carbon-carbon bond as the result of phenylation. These measurements are also valuable as a study of the specific heat of the benzene ring under varying conditions, and should furnish useful information for calculating the equilibrium constants of reactions involving phenylation.

The Method

The calibrated heat conduction method⁶ was selected because it offered the possibility of obtaining data of fair accuracy on a far larger number of compounds than would have been possible with the more precise but much slower method of intermittent electrical heating which has generally been used. The procedure consists essentially in passing heat into the substance through an insulating jacket across which a carefully controlled temperature head is maintained. The specific heat is calculated by comparing the rate of temperature rise with that of a standard substance heated under identical conditions. There is also the advantage with this method that no part of the temperature range is skipped in the observation and that any unusual thermal effects such as heats of transition are sure to be found.

The actual experimental data are in the form of rise in temperature, Δ microvolts, which takes place in the time interval, t seconds, during which the temperature head across the insulating jacket is ϕ microvolts; θ is the mean temperature of the substance during observation. Consequently the quantity, Q , will be proportional to the heat capacity of the calorimeter and its contents, letting $Q = \phi t / \Delta$. Table I gives the values of Q obtained at different temperatures in runs made at different times over a period of two months, illustrating the constancy of the calorimeter, after several improvements were made in the instrument as used by Andrews and Hawthorth.⁶

Because of the lower effective heat capacity per unit volume of the substances used in this investigation as compared with previous investigations, an effort was made to increase the accuracy of the calorimeter by more careful control of small errors.

The chief source of error appeared to be the water frozen on the shield at low temperatures or present either as liquid or vapor above 0°. Two runs were made with the calorimeter empty and glass beads in the insulating space. One was made under the usual conditions, while for the other a drop of water was put inside the shield and vaporized before cooling the calorimeter. The large difference in the results showed the considerable effect that a small amount of water on the surfaces of the calorimeter can and shield had on the determinations. In order to dry the surfaces and the air in the insulating space, two short pieces of small copper tubing were soldered into holes drilled in the cover of the insulating jacket and a current of air from a drying train was passed through the calorimeter before

each of the subsequent runs. These runs were all made without glass beads. A marked improvement in the results followed the use of this drying process.

In eliminating moisture from the calorimeter, another of the possible sources of error mentioned above was also removed. When the calorimeter was cooled, the gas taken into the insulating space was probably mostly oxygen from the liquid oxygen used for cooling. The thermal conductivities of oxygen and air differ enough to cause appreciable error if the composition of gas in the conduction space varies widely from run to run. By passing dry air through the calorimeter before and during the cooling process, it was insured that the gas in the conduction space was always the same.

Table I shows results obtained with 35.00 g. of triphenylmethane in four separate runs made over a period of two months. The procedure followed is described below. It is evident that the constants of the calorimeter did not change during this time. The average deviation of the individual results from the mean is about 0.35% or an extreme variation of 0.7%. This, together with comparisons made with data obtained by the Nernst method, indicates an accuracy of about 1% for the method. It must be emphasized that results as consistent as those shown in the table are obtained only by constant attention to the details of manipulation. The absolute accuracy of the results depends, of course, on the precision of the values used for the standard substance. A detailed description of the exact procedure follows.

The Modified Procedure

The material to be measured was packed into the can and the top to the can put in place. In transferring the material into the calorimeter a little fine dust usually settled between the can and shield. This was blown out with compressed air. In fact, every effort was made to keep the inner surface of the shield and outer surface of the can scrupulously clean. Between runs these surfaces were always washed with hot benzene and with ether.

After placing the cover on the shield, a current was passed through the heating coil. Dry air was at the same time passed inside the shield. The heating was continued for ten minutes or until the temperature of the shield had reached about 60°. About five minutes after the heating current was turned off the calorimeter was placed in a gallon Dewar flask and 1.5 liters of liquid air added as rapidly as possible. The current of air through the conduction space was continued until the can and material had reached liquid air temperature.

In addition to a soda-lime tower and two wash bottles of sulfuric acid in the air drying train, a liquid air trap was used next in line to the calorimeter.

After shutting off the current of dry air, the procedure was essentially the same as described by Andrews and Haworth in the papers cited.⁵

Calibration of the Apparatus

Calibrations were made with naphthalene, triphenylmethane, toluene and hydroquinone. The triphenylmethane results were not as consistent as the others. Toluene

was very good, but data were not available for higher temperatures. At temperatures both a little below and above the melting point of toluene this calibration gave results that were obviously erroneous. Two runs with hydroquinone gave very consistent results. Four runs with naphthalene were considered the most satisfactory and, since data on the heat capacity were available from several sources, that compound was chosen as the standard. The other compounds on which several runs were made served as a check on the accuracy of the method with different weights of material in the calorimeter.

Dr. R. F. Deese, Jr.,¹³ very kindly supplied data on naphthalene covering the temperature range from 90 to 300°K. These results were obtained with a Nernst type calorimeter. Huffman, Parks and Daniels³ have recently published a paper giving results on naphthalene over the same range. Andrews, Lynn and Johnston⁶ have given data for higher temperatures and the "International Critical Tables" give an equation for the specific heat over the range of -130° to the melting point. The values used for the heat capacity of naphthalene represent a combination of these data.

Runs were made on 30, 35, 40 and 45 g. of naphthalene and the resulting Q 's were plotted against the heat capacities for these weights at seventeen temperatures between 100 and 345°K. Only a few of the points were more than 0.5% from the best straight lines drawn through the four results for each temperature.

TABLE I
VALUES OF Q OBTAINED WITH 35.00 GRAMS OF TRIPHENYLMETHANE

Microvolts below °C.	Jan. 30	Feb. 21	March 6	March 30
5000	714	713	716	716
4500	868	865	867	869
4000	997	998	997	1001
3500	1116	1115	1114	1118
3000	1228	1224	1223	1227
2500	1330	1326	1327	1331
2000	1423	1422	1422	..
1500	1510	1513	1513	..
1000	1586	..	1590	..
500	1636	..	1638	..
0	1660	..	1664	..

Standards of Measurement.—The temperature scale used in these measurements is that established by Southard⁶ and is based on the e. m. f. of several constantan-copper thermocouples calibrated at fifteen different temperatures against two platinum resistance thermometers made by the Leeds and Northrup Company and calibrated by the Bureau of Standards (L. and N., Nos. 128,016, 137,184 and B. of S., Nos. 2736, 312). The accuracy of this scale was amply sufficient for the purpose. The potentiometer, standard resistances and general method of electrical measurement are the same as previously used by Southard and Andrews.⁶

Preparation of Materials

The polyphenyl hydrocarbons desired for this work were either unobtainable or rather costly, making it necessary to prepare the greater number of them. It was thought desirable to have about two hundred grams of each of the purified products, and,

¹³ Deese, private communication.

due to the shrinkage of the materials in the several steps of the preparations and purifications, working on a fairly large scale was essential.

Technical grades of such comparatively inexpensive starting materials as benzene, bromobenzene, benzoyl chloride, benzyl chloride and benzaldehyde were obtained in rather large quantities and purified. The hydrocarbons were all built up from these simple compounds. Since such intermediates as benzophenone, diphenylbromomethane, triphenylchloromethane and others could each be used in getting several different hydrocarbons, these were prepared in quantities of several kilograms. The preparation and properties of the intermediates are well known and will not be described further here except in cases where specific heat determinations have been made.

Compounds of the requisite purity for specific heat determinations are somewhat difficult to obtain. It is highly desirable that the mole percentage of impurities should not be more than one- or two-tenths where measurements are to be made in the region of the melting point of the eutectic formed between compound and impurity. But since the specific heats of related organic compounds do not differ greatly, 2% of impurities may be present and not seriously affect the results obtained on the liquid or on the solid well below the point of fusion.

Recrystallizations were carried out in the usual manner. Solids were air dried and also dried in a vacuum desiccator from one to two weeks.

The column used in the fractional distillations was 60 cm. long and was filled with 5-mm. glass tubing cut in lengths about equal to the diameter. Heat loss from the column was diminished by a high-vacuum jacket. This insulation was sufficient to permit distillations to be made at 125 to 150° without applying any heat to the column.

In all cases the distillations were carried out at reduced pressure so that the distillates came over at less than 130°. Dry carbon dioxide was passed in through the capillary in the distilling flask during all of the distillation.

A set of Anschutz thermometers was used for determining melting and boiling points. These were carefully checked against a new set of Bureau of Standards thermometers (B. S. Nos. 47,613 and 47,615).

Time-temperature freezing curves were made except in a few cases; these were taken as the final criterion of purity of the compounds.¹⁴

The record of source, method of preparation and of purification for the individual compounds is presented in the accompanying table. In the column headed "Source" the figures refer to the literature references which describe the source and method. "E. K. Co." refers to the Eastman Kodak Co.'s standard products.

In the column headed "Purification" the following notation is used: D, ordinary distillation; Dc, distillation from the column described above; S. D., steam distillation; Ca, recrystallization from alcohol; Cb, recrystallization from benzene; Ca_xb_y, recrystallization from *x* parts alcohol, *y* parts benzene.

Under "Melting point," "M. T." refers to the melting point determined in the ordinary way with a thermometer. "T. C." is the freezing point determined with a thermocouple. Under "Lit." are given the figures from the "International Critical Tables" (I) and from Beilstein's "Handbuch" (B).

Heat Capacities

Heat Capacities of the Phenyl Substituted Methanes.—The results of measurements on the four phenylmethanes are presented in Table III and Fig. 1.

The first three members of this series were compounds of unusual purity,

¹⁴ Andrews, Kohman and Johnston, *J. Phys. Chem.*, 29, 914 (1925).

TABLE II
 PREPARATION OF COMPOUNDS

Substance	Source	Purification	Melting point, °C.			Boiling point, °C.	Estimated impurities, %
			M. T.	T. C.	Lit.		
Toluene	E. K. Co.	Dc	-95.15	-95.1	...	0.1
Diphenylmethane	15	3D, 2Dc	25.0-25.1	25.15	I. 27	85-86 (1 mm.)	.1
Triphenylmethane	16	D, 3Ca, D	93.6-93.8	93.1	I. 92.5
Tetraphenylmethane	17	3Cb, D, 2Cb	283	I. 285
Ethylbenzene	Commercial	3Dc	...	-95.26	I. -92.81
1,1-Diphenylethane	18	D, Dc	...	-25.9	101-101.5 (2 mm.)	...
1,2-Diphenylethane	19	D, Ca, D, Ca, D, Ca, Dc	51.2-51.4	50.8	I. 52.5	95-96 (1 mm.)	.3
1,1,1-Triphenylethane	20	5Ca	94.8-95.0	94.3	B. 951
1,1,2-Triphenylethane	21	D, 4Ca	54.0-54.3	48.0	I. 54
1,1,1,2-Tetraphenylethane	22	Ca ₁ b ₁	143.5-143.7	141.1	B. 140-142
1,1,2,2-Tetraphenylethane	23	Cb, 2Cb _{2a} 1	211.4-211.7	210.4	I. 2095
Pentaphenylethane	24	Note A	173.0-173.5	I. 173
Phenylethylene	25	SD, 2Dc	...	-33.3	69.5-70 (60 mm.)	1.0
1,1-Diphenylethylene	26	D, 2Dc	...	8.2	I. 9	94-95 (1 mm.)	0.7
1,2-Diphenylethylene	27	D, 3Ca, D, 2Ca	124.5-124.8	123.9	I. 1245
Triphenylethylene	28	D, 6Ca	69.0-69.5	65.8	B. 62, 68
Tetraphenylethylene	29	6Cb	224.6-224.9	224.7	I. 2211
Phenylacetylene	30	3D, Dc	...	-44.8	142-143, I. 143	1.0
Diphenylacetylene	31	Note B	59-61	61.6	I. 60
Benzylchloride	E. K. Co.	4Dc	...	-39.7	I. -39	178.5 (754 mm.)	I. 179.4 0.5
Diphenylchloromethane	32	D, Dc	...	17.0	B. 12-14	113-114 (1.5 mm.)	1.5
Triphenylchloromethane	E. K. Co.	...	106-110	109.2	I. 112	...	2.5
Benzyl alcohol	E. K. Co.	-16.0	I. -15.3	85-85.5 (7 mm.)	1.0
Diphenylcarbinol	E. K. Co.	...	64-65	64.2	I. 68	...	2.0
Triphenylcarbinol	33	4Cb	162.4-162.5	162.2	I. 162.5	...	0.1

NOTE A.—This compound was prepared according to the directions of Gomberg and Cone from diphenylbromomethane and triphenylchloromethane by treatment with magnesium activated with iodine. Solution in benzene and precipitation with alcohol several times failed to remove the triphenylcarbinol present. The compound was then twice dissolved in benzene and precipitated with petroleum ether. After this treatment the product gave only a slight yellow color with concd. sulfuric acid, indicating the presence of only a trace of triphenylcarbinol.

NOTE B.—Stilbene in ether solution was treated with bromine and the resulting stilbene dibromide refluxed with an excess of alcoholic potassium hydroxide solution. The removal of the first hydrogen bromide was easily effected by this treatment, but the second required prolonged boiling of the mixture. The diphenylacetylene was distilled under reduced pressure and recrystallized six times from alcohol. The melting point was then two degrees lower than that given in the literature. Diphenylacetylene picrate was prepared and twice recrystallized from alcohol. The picrate was decomposed with dilute sodium hydroxide solution, and the hydrocarbon taken up in benzene and washed free of sodium picrate. The diphenylacetylene which had been through this process was finally recrystallized twice with alcohol.

and the tetraphenylmethane used, while perhaps not quite so pure, melts too high for this to have had an appreciable effect on the results. The purity of the compounds, together with the fact that three of them have recently been studied by other investigators, makes this series the best

TABLE III
MOLAL HEAT CAPACITIES OF THE PHENYL SUBSTITUTED METHANES

T, °K.	Toluene	Diphenyl- methane	Triphenyl- methane	Tetraphenyl- methane
	Calories per degree			
101.9	14.9	21.1	27.8	33.9
126.1	16.5	24.4	32.0	39.4
147.4	18.4	27.3	36.0	44.7
166.7	20.3	30.4	39.7	49.6
	Liquid			
184.4	31.7	33.2	43.4	54.7
201.1	32.2	36.2	47.1	59.1
216.8	32.6	39.3	50.6	63.0
231.7	33.1	41.7	53.9	67.7
246.0	33.9	44.3	57.2	71.4
259.8	34.6	47.1	60.4	75.4
273.1	35.6	49.9	63.8	79.9
286.0	37.0	52.7	67.0	84.0
298.5	38.7	55.8	70.6	88.0
		Liquid		
310.7		65.6	74.2	92.2
322.6		66.0	77.4	96.4
334.3			80.3	100.2
345.7			82.7	103.8

¹⁵ Friedel and Balsohn, *Bull. soc. chim.*, [2] **33**, 337 (1880).

¹⁶ "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. IV, pp. 81-83.

¹⁷ Ullman and Munzhuber, *Ber.*, **36**, 404 (1903).

¹⁸ Klages and Heilmann, *ibid.*, **37**, 1449 (1904).

¹⁹ Cannizzaro and Rossi, *Compt. rend.*, **53**, 541 (1861); *Ann.*, **121**, 250 (1862); Stelling and Fittig, *ibid.*, **137**, 258 (1866).

²⁰ Gomberg and Cone, *Ber.*, **39**, 1466, 2963 (1906).

²¹ Klages and Heilmann, *ibid.*, **37**, 1455 (1904).

²² Gomberg and Cone, *ibid.*, **39**, 1463 (1906).

²³ Norris, Thomas and Brown, *ibid.*, **43**, 2959 (1910).

²⁴ Gomberg and Cone, *ibid.*, **39**, 1467 (1906).

²⁵ "Organic Syntheses," 1928, Vol. VIII, pp. 84-86.

²⁶ "Organic Syntheses," 1926, Vol. VI, pp. 32-34.

²⁷ Hell, *Ber.*, **37**, 453 (1904).

²⁸ Hell and Wiegandt, *ibid.*, **37**, 1431 (1904).

²⁹ Engler and Bethge, *ibid.*, **7**, 1128 (1874); Boissieu, *Bull. soc. chim.*, [2] **49**, 681 (1888); Nef, *Ann.*, **298**, 237 (1897).

³⁰ Hessler, "Organic Syntheses," 1922, Vol. II, pp. 67-69.

³¹ Fittig, *Ann.*, **168**, 74 (1873).

³² Boeseken, *Rec. trav. chim.*, **22**, 312 (1903); Montagne, *ibid.*, **25**, 404 (1906).

³³ Acree, *Ber.*, **37**, 2755 (1904).

check obtained on the method. Three runs were made on toluene and the mean of the best two taken for the final values. The results for triphenylmethane represent the mean of three runs on different weights.

Kelley³⁴ has made very careful determinations of the heat capacity of toluene from 17°K. to room temperature. The mean deviation of thirteen points from a curve through his results was 1.3%. Huffman, Parks and Daniels³ have studied diphenylmethane and triphenylmethane. The mean deviation from their results was 0.9% for the first and 1.3% for the second compound. These deviations are not consistently in one direction.

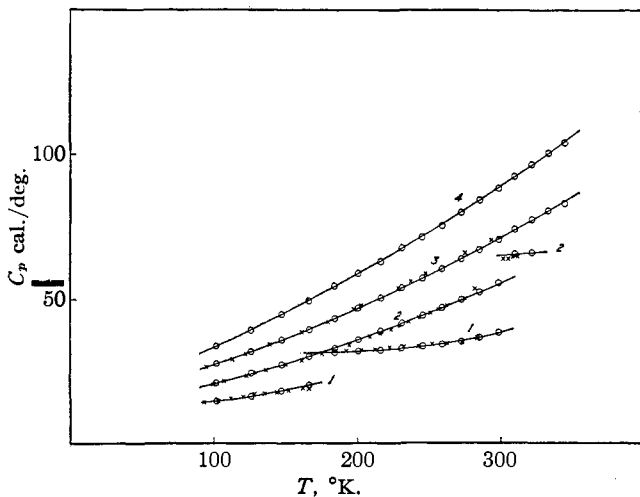


Fig. 1.—Molal heat capacities of the phenyl substituted methanes: 1, toluene; 2, diphenylmethane; 3, triphenylmethane; 4, tetraphenylmethane. The X's indicate results obtained on toluene by Kelley and those on diphenylmethane and triphenylmethane by Huffman, Parks and Daniels.

With both compounds the curves for the two sets of results cross once. Their results for diphenylmethane are, in general, lower and for triphenylmethane higher than those obtained in this work.

The heat capacity increment for a phenyl group in the series is practically constant at low temperatures. At higher temperatures the increment between the third and fourth members is somewhat larger than between the second and third. Unfortunately, the errors in the determinations may be accumulated in these increments and make any conclusions that may be drawn from a few compounds rather uncertain. The heat capacity of the phenyl group will be discussed further in considering the other series.

³⁴ Kelley, THIS JOURNAL, 51, 2738 (1929).

Heat Capacities of the Phenyl Substituted Ethanes.—With the possible exception of 1,1-diphenylethane, the purity of the materials for this series left little to be desired. The last point for solid 1,1-diphenylethane was taken from the extrapolated Q/θ curve.

TABLE IV
MOLAL HEAT CAPACITIES OF THE PHENYL SUBSTITUTED ETHANES

T, °K.	Calories per degree			
	Ethyl- benzene	1,1- Diphenyl- ethane	1,2- Diphenyl- ethane	1,1,1- Triphenyl- ethane
101.9	16.7	22.9	23.4	28.9
126.1	19.4	26.5	26.8	33.6
147.4	21.7	29.6	29.9	38.3
166.7	23.5	32.7	33.0	42.4
	Liquid			
184.4	36.3	35.4	36.0	46.6
201.1	37.3	38.7	39.1	50.7
216.8	38.0	41.8	42.1	54.6
231.7	38.7	44.8	45.0	58.1
246.0	39.8	Liquid	48.1	61.8
259.8	41.0	65.0	51.3	65.4
273.1	41.9	67.2	54.3	69.0
286.0	43.0	68.8	57.5	72.2
298.5	43.9	70.5	60.6	75.7
310.7				78.9
322.6				81.8
334.3				84.7
345.7				87.7

TABLE V
MOLAL HEAT CAPACITIES OF THE PHENYL SUBSTITUTED ETHANES

T, °K.	Calories per degree			
	1,1,2- Triphenyl- ethane	1,1,1,2- Tetraphenyl- ethane	1,1,2,2- Tetraphenyl- ethane	Penta- phenyl- ethane
101.9	29.0	35.4	36.7	43.0
126.1	34.2	41.7	42.7	50.1
147.4	39.0	47.0	48.4	56.3
166.7	43.3	51.8	53.4	62.2
184.4	47.7	57.1	58.7	68.0
201.1	51.4	62.0	63.9	74.2
216.8	55.1	67.3	68.4	80.4
231.7	58.7	71.7	72.9	85.9
246.0	62.3	76.2	77.4	91.5
259.8	65.8	81.1	82.2	97.0
273.1	69.2	85.8	86.9	102.5
286.0	72.7	90.1	91.0	107.8
298.5	76.4	94.5	94.8	113.2
310.7	80.2	98.9	98.4	119.3
322.6		103.0	102.1	124.1
334.3		107.5	106.0	128.1
345.7		111.6	110.0	130.5

Huffman, Parks and Daniels³ have also measured the specific heats of ethylbenzene and 1,2-diphenylethane. The mean deviations from their results are 1.5 and 1.4%, respectively, their results being, for the most part, higher.

The phenylethane series contains three pairs of isomers of a type not previously studied. The results indicate that the heat capacity of the more symmetrical isomer is higher in each case. However, the differences are of the order of the experimental error and more accurate measurements would

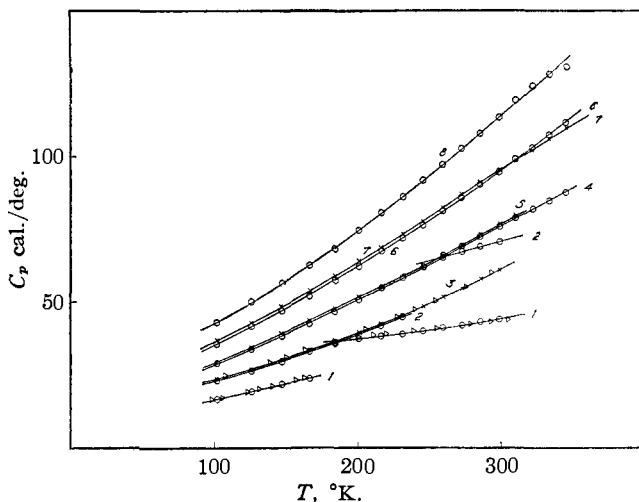


Fig. 2.—Molal heat capacities of the phenyl substituted ethanes: 1, ethylbenzene; 2, 1,1-diphenylethane; 3, 1,2-diphenylethane; 4, 1,1,1-triphenylethane; 5, 1,1,2-triphenylethane; 6, 1,1,1,2-tetraphenylethane; 7, 1,1,1,2-tetraphenylethane; 8, pentaphenylethane. The triangles show the data obtained by Huffman, Parks and Daniels on ethylbenzene and 1,2-diphenylethane.

be desirable for these compounds. Runs were made on the two tetraphenylethanes in May, 1929, and again in February, 1930. Differences of the same order were found on both occasions. The runs on the other pairs of isomers have not been repeated. In the case of the triphenylethanes, it is difficult to say which is the more symmetrical. The higher melting point of 1,1,1-triphenylethane would indicate greater symmetry for that compound. However, the heat capacity of 1,1,2-triphenylethane is slightly higher than that of 1,1,1-triphenylethane. With the three pairs of isomers it is, perhaps, better to say that there is an indication of slightly higher heat capacities for the isomers having the more even distribution of the phenyl groups around the ethane C-C bond.

The increments for the phenyl groups are surprisingly constant for the

symmetrical and for the unsymmetrical members of the series. The differences are, of course, more irregular if taken between a symmetrical and an unsymmetrical member. As in the phenylmethane series, there is a slight indication that the increment for the phenyl group is greater between the higher members of the series. The data obtained are tabulated in Tables IV and V and shown graphically in Fig. 2.

Heat Capacities of the Phenyl Substituted Ethylenes.—The increment for the phenyl group in this series is fairly constant for a given temperature and is about the same as found for the methanes and ethanes. The heat capacities of the ethylenes are slightly lower, especially at higher temperatures, than those of the corresponding ethanes. This might be attributed to the greater strength of the double bond, but, since these differences are only about 2 or 3% at 300°K., such a conclusion would be quite uncertain. It will be observed that the results for 1,1-diphenylethylene are appreciably higher than for the symmetrical isomer. This is the reverse of what was found for the ethanes.

With the exception of phenylethylene, the purity of the materials used for the determinations in this series was satisfactory. Marked premelting of the phenylethylene made it impossible to obtain any results over a considerable range below the melting point. In fact, the accuracy of all the data on this compound is questionable.

Table VI shows the results for the phenyl compounds of ethylene.

TABLE VI
MOLAL HEAT CAPACITIES OF THE PHENYL SUBSTITUTED ETHYLENES

T, °K.	Phenyl- ethylene	Calories per degree			
		1,1- Diphenyl- ethylene	1,2- Diphenyl- ethylene	Triphenyl- ethylene	Tetraphenyl- ethylene
101.9	15.6	22.3	21.8	29.1	37.0
126.1	18.9	26.3	25.4	33.9	43.0
147.4	21.9	29.8	28.8	38.1	48.6
166.7	24.5	33.3	32.0	42.3	53.2
184.4	..	36.6	35.1	46.4	58.1
201.1	..	39.4	38.1	50.5	63.2
216.8	..	42.2	40.8	54.5	67.6
231.7	Liquid	44.9	43.1	57.3	71.6
246.0	39.7	47.7	45.6	60.6	75.6
259.8	40.4	50.7	48.1	63.9	79.8
273.1	41.1	Liquid	50.8	67.3	83.5
286.0	41.9	70.1	53.1	70.4	87.8
298.5	43.0	71.5	55.6	73.9	92.5
310.7			58.1	77.5	96.4
322.3			60.3	80.7	100.3
334.3			62.6		103.8
345.7			64.5		107.2

Heat Capacities of the Phenyl Substituted Acetylenes.—The data are given in Table VII. There being only two members of this series, fewer

comparisons can be made. The phenyl group increment is about the same as was found for the three foregoing sets of compounds. The heat capacity of diphenylacetylene at higher temperatures is slightly lower than that of the corresponding ethylene. Here again the difference is in the direction expected, but it is scarcely greater than the possible error in the measurements.

TABLE VII
MOLAL HEAT CAPACITIES OF THE PHENYL SUBSTITUTED ACETYLENES

T, °K.	Phenyl- acetylene		T, °K.	Phenyl- acetylene	
	Calories per degree			Calories per degree	
101.9	15.0	21.7	231.7	38.9	42.2
126.1	17.3	24.8	246.0	39.5	44.5
147.4	19.4	28.0	259.8	40.0	47.0
166.7	21.4	31.3	273.1	40.7	49.2
184.4	23.3	34.3	286.0	41.7	51.6
201.1	25.1	37.2	298.5	42.9	54.0
216.8	26.9	39.7	310.7		56.4
			322.6		58.5

Heat Capacities of the Phenyl Carbinols.—Of the three compounds in this series, only the triphenylcarbinol was obtained in a state of really satisfactory purity for thermal measurements. With benzyl alcohol a small "hump" was observed in the Q/θ curve between 150° and 200°K. The readings appeared to be normal above and below this region and the heat capacity was calculated from a smooth curve which disregarded the irregular points. It seemed quite probable that these were due to the melting of a small amount of impurities.

TABLE VIII
MOLAL HEAT CAPACITIES OF THE PHENYL CARBINOLS

T, °K.	Calories per degree		
	Benzyl alcohol	Diphenylcarbinol	Triphenylcarbinol
101.9	14.6	21.2	29.2
126.1	17.5	25.0	34.5
147.4	20.1	27.7	39.1
166.7	22.2	31.3	43.6
184.4	24.2	34.3	47.8
201.1	26.1	37.4	51.7
216.8	27.9	40.3	55.4
231.7	29.7	42.9	59.0
246.0	Liquid	45.7	62.5
259.8	45.3	48.2	66.1
273.1	47.9	50.8	69.6
286.0	49.9	53.7	72.9
298.5	51.6	56.6	76.2
310.7			79.4
322.6			82.4
334.3			85.1
345.7			87.7

The heat capacity increment between di- and triphenylcarbinol over the whole temperature range is consistently 2 to 3 calories higher than it is between diphenylcarbinol and benzyl alcohol.

The data are represented in Table VIII.

Heat Capacities of the Phenylchloromethanes.—The differences in the heat capacities between the second and third members of the series is 2 or 3 calories greater than that between the first and second. This is again in the direction that would be expected if the valence force between carbon and chlorine is decreased with the addition of the phenyl groups.

Unfortunately, the purity of the materials used for measurements in this series was not so good. The benzyl chloride was the best of the three. Table IX gives the results obtained.

TABLE IX
MOLAL HEAT CAPACITIES OF THE PHENYLCHLOROMETHANES

T. °K.	Benzyl chloride	Diphenylchloromethane	Triphenylchloromethane
	Calories per degree		
101.9	17.3	23.6	29.5
126.1	19.7	26.8	34.8
147.4	22.2	29.8	39.3
166.7	24.5	32.8	43.2
184.4	26.7	35.6	47.2
201.1	28.8	38.4	51.0
216.8	..	41.2	55.0
231.7	Liquid	43.5	58.3
246.0	41.4	46.3	61.6
259.8	42.1	49.2	64.6
273.1	42.5	51.8	67.7
286.0	43.1	Liquid	70.9
298.5	43.6	69.4	74.5
310.7		70.7	78.1
322.6			80.9
334.3			83.4
345.7			85.3

Conclusions

The conclusions to be drawn from the data reported here fall naturally into two groups, those of thermodynamic interest such as the calculation of entropy, and free energy, and those of kinetic interest such as the study of the distribution of thermal energy among the different parts of a molecule. Since it is necessary in making the thermodynamic calculations to extrapolate the curves to absolute zero, these calculations will not be discussed until the new methods of extrapolation based on Raman spectra have been presented in a later paper. The conclusions of kinetic interest are also closely related to the structure of the molecule as revealed by Raman spectra, but in connection with them it is perhaps worth while to point out a few facts of general significance which may be deduced directly from the data.

One of the principal reasons for the study of this series lies in the hope that some light may be thrown on the change in the ethane carbon-carbon bond which seems to take place, according to the chemical evidence, as we load down the molecule with phenyl groups. From the fact that in triphenylmethyl this carbon-carbon bond is completely severed, we might expect that a progressive weakening would take place as we go down the series. If this were true, there should be a decrease in the frequency of vibration of all the types of motion which involve this bond and the heat capacity due to such vibrations should be increased.

The easiest way to look for such an effect, without making a careful analysis of all the terms involved (as will be done later), is to look for a change in the increment in heat capacity caused by the addition of a phenyl group as we proceed down the series. It is true that if the addition of each succeeding phenyl group caused the same increase in loosening of the carbon-carbon bond, the increments in heat capacity might be the same for each successive addition and the effect would be masked. However, since the frequency (ν) varies as the square root of the force constant (k) of the bond

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (1)$$

(μ is a function of the mass) and since the specific heat is an exponential function of the frequency, such an effect is hardly to be expected. Moreover, we can compare the increment due to the phenyl group in the ethane series to the increment in the methane and other series where there is no possibility of a similar loosening effect.

Table X shows the increments in heat capacity which are found between different members of the two series. The approximate constancy of the increment at any given temperature is at once apparent. There is only a slight tendency for it to increase appreciably toward the end of the series, and it is essentially the same in all the different series. This seems to point definitely to the fact that the force constant of the bond is not greatly affected and that the heat capacity of the phenyl radical is quite independent of its environment in these groups.

This, of course, does not prove that the *breaking* of the carbon-carbon bond is not rendered easier by phenylation. Since the strength of the bond is defined in so many different ways, a word may perhaps be in order to distinguish clearly the difference between the *force constant* or *elastic constant* and the *chemical strength* or *heat of linkage*. Figure 3 shows the way the force of a single normal bond varies with the separation of the two carbon atoms which it joins.³⁵ When they are 1.5 Å. apart, equilibrium distance, there is no force acting between them. Closer than this they are repelled; further apart, they are attracted with a force which, however,

³⁵ D. H. Andrews, "Colloid Symposium Annual," 1930, p. 119.

TABLE X
HEAT CAPACITY INCREMENTS FOR ADDITION OF A PHENYL GROUP, CAL./DEG.

	120°	220°	320°
Toluene	7.5
Diphenylmethane	7.5	11.6	..
Triphenylmethane	7.1	12.9	19.0
Tetraphenylmethane			
Ethylbenzene	6.8
1,1-Diphenylethane	7.2	12.9	..
1,1,1-Diphenylethane	7.3	12.9	21.0
1,1,1,2-Tetraphenylethane	8.0	13.4	20.3
Pentaphenylethane			
Ethylbenzene	7.2
1,2-Diphenylethane	7.2	13.0	..
1,1,2-Triphenylethane	8.1	13.8	..
1,1,2,2-Tetraphenylethane	6.8	12.1	21.0
Pentaphenylethane			
Phenylethylene	7.3
1,1-Diphenylethylene	7.4	12.4	..
Triphenylethylene	8.9	13.3	19.6
Tetraphenylethylene			
Phenylethylene	6.3
1,2-Diphenylethylene	8.3	13.8	20.3
Triphenylethylene			
Phenylacetylene	7.3	12.9	..
Diphenylacetylene			

goes through a maximum and becomes practically zero as the distance between them is increased to the point where they are "dissociated." Now the vibrations which determine the heat capacity in the case we have been

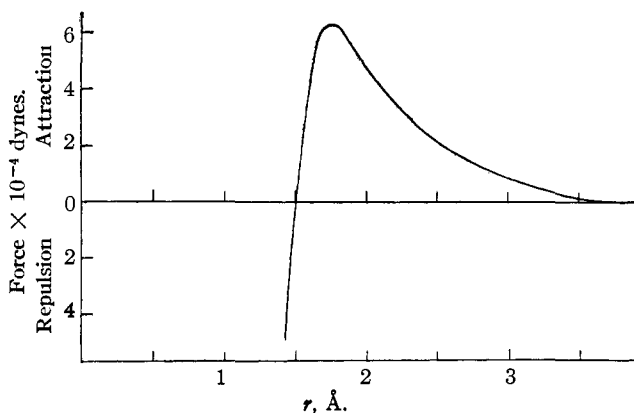


Fig. 3.—The force of a single homopolar bond operating between two carbon atoms separated by distance r , according to the Morse wave mechanics function (Ref. 35).

studying take place with an amplitude of only a few tenths of an Å. about the equilibrium position. The force constant (k) in Equation 1 is the slope of the curve in Fig. 3 in the neighborhood of the equilibrium position. We can, therefore, say that in the normal state of the molecule, at the temperatures considered, phenylation has not greatly affected the bond in respect to its *force constant*. As regards chemical activity, however, it is evident from the figure that to pull the molecule to pieces and form a new chemical compound, one must overcome the force in the region of the maximum and beyond. We can get evidence about the nature of this part of the curve from the heat of dissociation, since the latter is the integral represented by the area under the curve from the equilibrium point to dissociation, that is, where the force drops to zero again. There is reason to believe that the heat of dissociation does fall off with increasing phenylation. In other words, as we pull the molecule apart and distort the electron configuration, we find phenylation has a decided effect on molecular behavior, although in the undistorted molecule the addition of phenyl groups does not seem to affect the ethane C-C linkage.

These conclusions are in accord with the idea that the normal homopolar chemical bond is a definite structural unit and that its properties are relatively independent of the nature of the atoms which it joins or the other atoms near it, if the atomic weights are not higher than about twenty. This concept of the bond first took concrete form in Lewis's suggestion that the bond is made up of a pair of electrons. The quantitative evidence from spectra and heat capacities substantiates this hypothesis^{7,8} and the results presented here seem to be in good agreement with it.

Summary

1. The accuracy of the measurement of heat capacity by the method of calibrated heat conduction has been improved.
2. The heat capacities of phenyl derivatives of methane and ethane and thirteen related compounds have been measured from 100 to 320°K.
3. An analysis of the data indicates that in the normal or unexcited molecule there is very little decrease in the force of the ethane carbon-carbon bond upon phenylation. This favors the idea that the bond is a definite structural unit relatively independent of its environment.

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