

In the third experiment, one electrode was placed opposite a flat disk of Bakelite in the boric acid solution under oxygen. It was found that the potential was affected when the electrode was 0.2 mm. from the Bakelite and when brought up against it the potential changed 147 millivolts. This distance is also of the order of one-half that between two electrodes when the potential was affected in the same solution.

Summary

It has been shown that when two parallel platinum electrodes are brought together in certain solutions in contact with oxygen or air, the potential changes with the distance between the electrodes. This phenomenon is considered supporting evidence to a theory that the potential is due in part to an adsorbed ionic film extending from the electrode a measurable distance out into the solution.

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THE HEATS OF VAPORIZATION OF SOME ORGANIC COMPOUNDS

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The electrical method for the determination of heats of vaporization which was developed in this Laboratory,¹ has been further improved by changes in both design of apparatus and technique of operation. In this article we shall briefly describe these changes, and give the results of new determinations.

The method (for complete description see original article) consists essentially of a determination of the exact time necessary for the vaporization of a predetermined definite weight of liquid contained in the vaporizing tube (B, Fig. 1) by a precisely maintained supply of electrical energy passing through the heating coil, L, the tube containing the liquid being suspended in a vapor thermostat to prevent heat losses. The vaporizer tube, B, is nearly filled with the liquid being studied and a portion of the same liquid is placed in the "boiler" below, containing the heating coil, H. Vapor rises from the boiling liquid below and completely envelops the vaporizer tube, the excess passing out at the top of the chamber, C, into the outer chamber, D, and thence back through the condenser and trap to the "boiler" below.

The liquid in the vaporizer is heated by a current maintained at exactly 1 amp. and after thermal equilibrium has been established throughout the

¹ J. H. Mathews, *THIS JOURNAL*, **48**, 562 (1926).

system a definite weight of liquid, usually 10 g. is evaporated, the exact time necessary for evaporation being noted. It is believed that this procedure, which does not require an interruption of the boiling process, is better than certain former procedures in which the boiling was discontinued in order to make the necessary weighings. In the procedure here used the boiling of the liquid in the vaporizer is adjusted to a constant rate in the preliminary period and is constantly maintained at this same rate throughout. An interruption of boiling is undesirable as it often results in superheating of the liquid when the current is again turned on. Frequently this superheating, due to delayed ebullition, is sufficient to eject most of the liquid in the tube when boiling does start. The procedure here used avoids such difficulty and at the same time accurate weighings are secured.

Changes in Apparatus.—For the work recorded in the present paper the entire apparatus was redesigned (Fig. 2) for the purpose of reducing the amount of liquid necessary for a series of determinations, as many of the liquids were not available in sufficient quantity (100 to 150 cc. of pure material) for the old form of apparatus. At the same time the cork ring, K (Fig. 1), was eliminated and an inner seal substituted therefor, with a ground glass joint above. The cork frequently was attacked by the liquids used and sometimes was softened to such an extent as to produce leaks. It was always a possible source of contamination of the liquids and its use always resulted in a considerable wastage of material—all of which is obviated by the use of an inner seal. The “boiler” was greatly reduced in size, to permit a considerable reduction in the amount of liquid used in the isothermal control. As vaporization proceeds from the vaporizer small amounts of liquid are tapped off from time to time through the stopcock at the bottom.

The vaporizer tube itself was blown from Pyrex, hence the heavy platinum leads were replaced by tungsten, to which the platinum heating coil wires were gold-soldered inside the tube. The former copper “contactors” which dipped into the mercury cups were replaced with No. 26 gage platinum wires, which were german silver-soldered to the ends of the tungsten leads. To insure good contact a very small ball of gold-platinum alloy

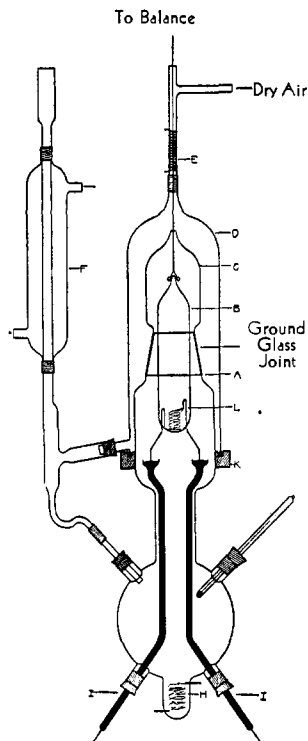


Fig. 1.

was fused on the end of each platinum "contactor," care being taken to use only enough gold in the alloy to enable wetting by mercury to take place. In making a run these contactor balls were submerged several millimeters below the mercury surface in the cups, thus avoiding the surface tension effect and insuring sensitive weighing.

The silvering of the jacket was dispensed with, as it was found that many liquids attacked and loosened the mirror. The amount of heat lost by radiation without the silver reflecting surface is negligible, as shown by the following data, in which the heat of vaporization of benzene was determined in both forms of apparatus.

SILVERED FORM OF APPARATUS		
Observer	Temperature, °C.	L, calories per gram
Ramsdell, in 1923	80.2	94.31
Thompson, in 1924	80.2	94.35
UNSILVERED FORM OF APPARATUS		
Fehlandt, in 1930	80.2	94.34

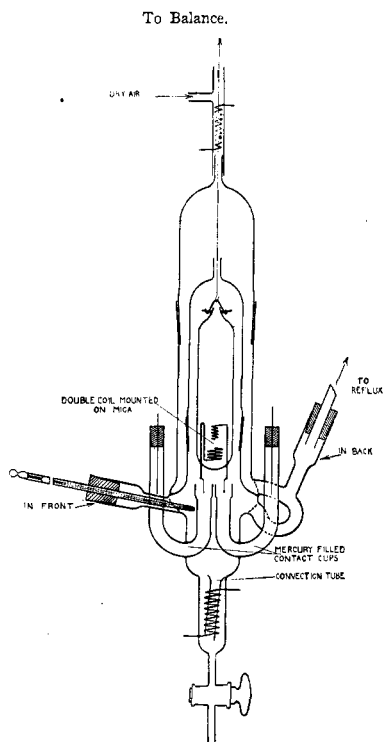


Fig. 2—The thermometer and reflux tubulars shown thus, for simplicity, are in the plane perpendicular to this.

The most noteworthy improvement, however, was in the smaller size of the "boiler." The previous globe-form required larger quantities of liquid than were often available; therefore the new "boiler" was diminished essentially to a well 18×55 mm., sufficient in size to hold the vaporizer coil; 15 ml. of liquid is sufficient to fill the "boiler" for a run, but as extra liquid would distil out from the vaporizer and be returned to the boiler by the reflux, a stopcock to draw off the excess was provided at the bottom of the boiler. The small size of the well itself provided no room for the mercury lead tubes, thermometer tubulure and condenser return tube, so they were sealed through the swelled glass portion just above the well.

This convenient and compact form of apparatus gave results almost identical with, and presumably as accurate as, the older type, yet required only 30 ml. of benzene for a run, as compared with 110 ml. for the older form.

Changes in Procedure.—The resis-

tance of the terminals external to the vaporizer coil could no longer be calculated conveniently, so it was determined directly. The two-way switch placed the potentiometer in circuit with the vaporizer coil (through a 50.018 to 1 volt box) and the resultant reading with 1.0000 ampere of current flowing gave the resistance of the entire circuit—connecting wires, mercury cups, "contactors," tungsten leads and vaporizer coil. The vaporizer coil was then short-circuited by wrapping 40 turns of freshly sanded No. 36 copper wire around the projecting tungsten leads close to the vaporizer. With all other conditions the same as before, the new potentiometer reading gave the resistance of that part of the circuit external to the heating coil proper. The difference between these readings gave the resistance of the coil alone.

The other principal change consisted simply in thoroughly drying the vaporizer coil (previously platinized) before each run. This drying was most advantageously done by passing about 0.35 ampere through the coil while dry air was gently blown over it. From ten to thirty minutes sufficed, depending on the liquid previously used. The effect of the drying was to give even boiling without superheating, and hence good current control and regular resistance readings on the vaporizer coil. The importance of this drying is shown by the following runs on benzene, the values given being the resistance in ohms of the vaporizer coil, taken through the 50.018 to 1 volt box.

VAPORIZER COIL NOT DRIED BETWEEN RUNS

March 12.	Six successive runs under identical conditions gave				
0.12885	0.12917	0.12874	0.12925	0.12960	0.12892
Mean, 0.12909.	Average deviation from mean, 0.00025				
April 2.					
0.13198	0.13273	0.13160	0.13224	0.13232	
Mean, 0.13217.	Average deviation from mean, 0.00033				

VAPORIZER COIL DRIED BETWEEN RUNS

April 12.				
0.13046	0.13050	0.13048	0.13043	
Mean, 0.13047.	Average deviation from mean, 0.00002			
April 13.				
0.13090	0.13089	0.13089	0.13091	
Mean, 0.13090.	Average deviation from mean, 0.00001			
April 14.				
0.13099	0.13099	0.13100	0.13101	
Mean, 0.13100.	Average deviation from mean, 0.00001			

These figures clearly show the importance of drying the coil before runs in order to get uniform values for the vaporizer coil resistance.

As to why the drying promotes even boiling, it is believed that the platinum black surface on the coil wire contains a multitude of minute interstices which can act as capillary boiling tubes. Drying drives out all liquid

and fills the interstices with air so the boiling tubes can function. Allowing the apparatus to cool between runs will cause liquid to be sucked into the tiny capillaries and their efficiency as boiling tubes is then destroyed, unless the platinum black is thoroughly dried again.

Substance	PURIFICATION OF MATERIALS			B. p. (760 mm.), °C.
	Source	Method of purification		
Acetyl bromide	Eastman Kodak Co.	10 fr., Vigreux stillhead		75.9-75.95
Acetyl chloride	Baker and Adamson	6 fr., Hempel stillhead		50.08-50.12 (at 741 mm.)
<i>n</i> -Amyl chloride	Eastman Kodak Co.	4 fr. Hempel column		105.8-106.3
<i>Tert.</i> -amyl chloride	Eastman Kodak Co.	Dried P ₂ O ₅ , 4 fr. Vigreux column		85.05
<i>n</i> -Butyl bromide	Eastman Kodak Co.	Dried CaCl ₂ , 4 fr. Vigreux column		101.4
<i>n</i> -Butyl chloride	Eastman Kodak Co.	Dried P ₂ O ₅ , 4 fr. Hempel column		77.5-77.9
<i>n</i> -Butyl ether	Eastman Kodak Co.	Dig. CaO, washed H ₂ O, dried CaCl ₂ , refl. Na, fr. 5 times, Hempel column		142.2-142.4
Cyclohexanol	Eastman Kodak Co.	Dig. CaO, fr. 2, Hempel column		158.7-159.4 (737 mm.)
Diethylaniline	Kahlbaum	Fr. 4 times from zinc dust and Na		216.3-216.9
Di-isobutylene	Wis. lab.	Wash H ₂ O, dried CaCl ₂ , fr. several times		102.7-102.9
Dimethylaniline	Kahlbaum	Fr. 4, Vigreux column		192.0-192.5
Furan	Miner Lab.	Shake 1% NaOH, and refr.		31.32-31.35
Furfuryl acetate	Miner Lab.	5 Refr.		182.0-182.4
Isoamyl bromide	Eastman Kodak Co.	5 fr. Hempel column		121.3-121.6
Isopropyl bromide	Eastman Kodak Co.	3 fr. Vigreux column		59.2-59.8
Isopropyl chloride	Eastman Kodak Co.	3 fr. Vigreux column		36.0
Methyl amyl ketone	N. W. Univ. lab.	Dried CaCl ₂ , fr.		150.40-150.42
Methylaniline	Kahlbaum	Fr. 4 times		194.5-195.0
Methyl furoate	Miner Lab.	Fr. 4 times		181.8-182.1
<i>n</i> -Propyl bromide	Eastman Kodak Co.	Fr. 4 times		70.6-70.7
<i>n</i> -Propyl chloride	Eastman Kodak Co.	Fr. 4 times		45.70-45.75
Triisobutylene	Wis. Univ.	Refr.		174.4-174.6

RESULTS OF MEASUREMENTS

Substance	Number of detns.	Temp., °C.	<i>L</i> , in cal. per g.	Mean probable error	Observer
Acetyl bromide	3	75.1	58.99	±0.08	Fehlandt
Acetyl chloride	7	50.4	87.14	±.09	Fehlandt
<i>n</i> -Amyl chloride	5	105.0	74.41	±.03	Fehlandt
<i>Tert.</i> -amyl chloride	4	83.2	68.89	±.09	Wendt
<i>n</i> -Butyl bromide	4	99.4	56.76	±.08	Wendt
<i>n</i> -Butyl chloride	4	76.5	79.77	±.04	Fehlandt
<i>n</i> -Butyl ether	5	141.3	67.80	±.03	Fehlandt
Cyclohexanol	2	158.7	108.58	±.03 ^a	Fehlandt
Diethylaniline	5	215.2	74.15	±.28	Fehlandt
Di-isobutylene	6	101.3	67.93	±.12	Maresh

RESULTS OF MEASUREMENTS (Concluded)

Substance	Number of detns.	Temp., °C.	L, in cal. per g.	Mean probable error	Observer
Dimethylaniline	5	192.7	87.48	±0.06	Wendt
Furan	4	31.2	95.50	±.02	Keenan
Furfuryl acetate	9	181.2	77.90	±.12	Maresh
Isoamyl bromide	3	121.6	57.84	±.30 ^b	Fehlandt
Isopropyl bromide	3	58.6	55.19	±.09	Fehlandt
Isopropyl chloride	11	34.0	80.68	±.11	Wendt
Methyl amyl ketone	4	149.2	82.70	±.02	Keenan
Methylaniline	7	193.6	101.20	±.23	Wendt
Methyl furoate	8	181.8	84.18	±.13	Maresh
<i>n</i> -Propyl bromide	6	68.8	58.02	±.12	Wendt
<i>n</i> -Propyl chloride	4	45.7	84.32	±.26	Wendt
Tri-isobutylene	6	174.4	57.54	±.15	Maresh

^a The smallness of the sample permitted only two runs; hence, 0.3 represents only deviation of each run from the mean. To calculate mean error by the method of least squares, at least three values are needed. ^b Some decomposition took place.

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Summary

1. The latest improvements in apparatus and procedure for the Mathews' electrical method of determining heats of vaporization have been given.

2. The heats of vaporization of twenty-two compounds have been determined and their values stated.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

BASIC CATALYSIS IN THE DECOMPOSITION OF DIACETONE ALCOHOL

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In alkaline solution diacetone alcohol decomposes according to the equation $C_6H_{12}O_6 \longrightarrow 2(CH_3)_2CO$. Koelichen¹ showed that for solutions originally containing less than 5% diacetone alcohol the equilibrium was so far displaced toward the acetone that the decomposition might be considered a monomolecular reaction proceeding to completion. Furthermore, he found that for concentrations of alkali hydroxide below 0.1 *N*, the rate of reaction was proportional to the concentration of hydroxyl ion, and suggested that the reaction might be used to determine the dis-

¹ Koelichen, *Z. physik. Chem.*, **33**, 129 (1900).