

Anal. Subs., 0.5470, 0.2182: toluene (by loss of weight), 0.0561, 0.0226. Calcd. for $C_{10}H_{14}N_2$, $C_6H_5CH_3$: $C_6H_5CH_3$, 10.40. Found: 10.25, 10.35.

For the numerous preparations described in this paper I have to express my thanks to my assiduous collaborators, Dr. F. de Montmollin, Dr. F. Abouchy, Dr. R. Bretagne, R. Mercanton, chim. dipl., Dr. E. Oppenheim and C. Pedrazzini, ing. chim. dipl., with whom I worked at the University of Lausanne.

Summary

A certain number of biphenyl derivatives of *p*-phenylenediamine and of benzidine have been prepared and described, as well as their meriquinonic salts. At the same time different biphenyl derivatives of ammonia have been prepared, which had not previously been made and which were necessary for the present work.¹⁶

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]
**THE VAPOR PRESSURES, DENSITIES, AND SOME DERIVED
QUANTITIES FOR ACETONE**

BY W. A. FELSING AND S. A. DURBAN

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Introduction

In an investigation dealing with certain addition compounds of sodium iodide with acetone it became desirable to know accurately the vapor pressures of acetone at various temperatures, more especially at low temperatures. An examination of the literature pointed toward the necessity of checking the existing data from about -80° to $+60^\circ$. Incidental to this investigation was a determination of the densities of liquid acetone over the same temperature range. An outside request was made for data on the solubility of carbon dioxide in acetone over the temperature range -75° to $+25^\circ$. These data are also included.

Regnault¹ measured the vapor pressures of acetone from 20° to 140° . Taylor² covered practically the same range. Drucker, Jiménez and Kangro³ investigated the range -94.8° to 10.7° . Sameshima⁴ presents data, undoubtedly "smoothed out," from 5° to 50° . N. Jacob⁵ bridges the gap

¹⁶ In another paper [*Ber.*, 59, 1438 (1926)] will be found a discussion of the constitution formula of the meriquinonic salts. This has not been touched on in the present article.

¹ Regnault, *Mém. Paris*, 26, 339 (1862).

² Taylor, *J. Phys. Chem.*, 4, 366 (1900).

³ Drucker, Jiménez and Kangro, *Z. physik. Chem.*, 90, 518 (1915).

⁴ Sameshima, *THIS JOURNAL*, 40, 1488 (1918).

⁵ Jacob, *Recherches et Inventions*, N. S. [II] 12, 460 (1924).

from -20° to $+20^{\circ}$; and Price⁶ cites eight determinations from 20° to 50° . Numerous isolated vapor-pressure data as well as boiling-point values at definite barometric pressures, too, are found⁷ in the literature. These data were obtained in a number of types of apparatus with various degrees of accuracy; they are often quite discordant, but seem to be as accurate as the apparatus, temperature control, purity of the acetone, etc., would permit.

Quite a number of density data are available, chiefly at 20° . The only series determinations seem to be due to Archibald and Ure,⁸ using a modified Ostwald-Sprengel pycnometer over the range -89.7° to 0° ; to McElroy and Krug,⁹ who measured the density from 15° to 25° ; to Price,⁶ who measured it from 20° to 50° in 10° intervals; and to Bramley¹⁰ who measured it over the same range. Numerous isolated data are found,¹¹ among which considerable discordance is noted.

Method and Apparatus

The vapor-pressure determinations were divided into two series, employing slightly different types of apparatus: one series above zero and one below zero. The types of apparatus will be described in so far as they differ essentially; the same loading apparatus was employed throughout.

The Thermometers.—For temperatures *above* 0° , mercury thermometers of short range and calibrated by the United States Bureau of Standards were employed. These thermometers could be read accurately to 0.02° . For temperatures *below* 0° , a platinum resistance thermometer of the flat coil, silver sheath, potential type was employed. This thermometer had also been calibrated between 0° and 100° by the Bureau of Standards. This thermometer was used with a Type K, Leeds and Northrup potentiometer (and accessories) together with a 10-ohm standard resistance of the Bureau of Standards type. The resistance was accurate to 0.01%.

In order to use the thermometer at low temperatures, it was calibrated at the boiling point of oxygen, at the sublimation point of carbon dioxide, and at the freezing point of pure mercury by the method of Keyes, Town-

⁶ Price, *J. Chem. Soc.*, **115**, 1116 (1919).

⁷ (a) Linnemann, *Ann.*, **161**, 59 (1872). (b) Beckmann and Faust, *Z. physik. Chem.*, **89**, 238 (1914). (c) Perkin, *J. Chem. Soc.*, **45**, 478 (1884). (d) v. Zawidzki, *Z. physik. Chem.*, **35**, 129 (1900). (e) Timmermans, *Bull. soc. chim. belg.*, **24**, 244 (1910). (f) Richards and Shipley, *THIS JOURNAL*, **38**, 996 (1916).

⁸ Archibald and Ure, *J. Chem. Soc.*, **125**, 726 (1924).

⁹ McElroy and Krug, *J. Soc. Chem. Ind.*, **12**, 177 (1893).

¹⁰ Bramley, *J. Chem. Soc.*, **109**, 455 (1916).

¹¹ (a) Shipsey and Werner, *J. Chem. Soc.*, **103**, 1255 (1913). (b) Lowry, *ibid.*, **105**, 81 (1914). (c) Timmermans, *Proc. Roy. Soc. Sci. Dublin*, **13**, 330 (1912). Ref. 7 e; (d) *Bull. soc. chim. belg.*, **26**, 205 (1912). Ref. 7 c. (e) Linnemann, *Ann.*, **143**, 349 (1867); (f) **161**, 59 (1872). (g) Squibb, *THIS JOURNAL*, **17**, 200 (1895). Ref. 7 f.

shend and Young.¹² The boiling point (760 mm.) of oxygen was taken as -182.94° ; the sublimation point (760 mm.) of carbon dioxide as -78.53° and the melting point of pure mercury as -38.90° . In determining the boiling point of oxygen and the sublimation point of carbon dioxide, the values of dp/dT were calculated from the data of Cath¹³ and from the data of Henning.¹⁴ The observed resistances of the thermometer were plotted on a large scale against the absolute temperatures; the equation for this empirical relation was found to be

$$T = 33.600 + 9.3319 R - 26.39 \times 10^{-3} R^2 + 11.96 \times 10^{-4} R^3 \quad (1)$$

All temperatures were calculated from observed resistances by means of this relation.

The Cryostats.—For temperatures above 0° , the apparatus of Fig. 1 was employed. The cryostat liquid was a mixture of kerosene and liquid paraffin; the heating element consisted of No. 24 (B. and S.) "Karma" wire wound on a Pyrex tube; the current was hand-regulated. Cooling was effected by copper cooling coils supplying cold brine from a reservoir. The whole apparatus was contained in a highly evacuated, silvered Pyrex Dewar flask of 10 cm. internal diameter. A "seal through" connection allowed a direct connection of the interior to the exterior manometer arm.

For temperatures below 0° the cryostat described by Taylor and Smith¹⁵ was at first used. It was found difficult, however, to keep the temperature constant over the time interval required to attain equilibrium in the acetone system. The cryostat arrangement finally adopted was that described by Walters and Loomis.¹⁶ With this arrangement excellent constancy was obtained. The cryostat liquid was ethyl bromide.

The Manometers.—The principal manometer was of the type described by Taylor and Smith;¹⁵ for the lowest temperatures a calibrated, large-capillary McLeod gage was employed. In measurements above 0° , the arm *B* of their apparatus was placed inside the cryostat, as shown in our Fig. 1. The corrections for the difference in density in the outer and inner arms, due to temperature differences, were made in the usual manner. In measurements below zero, both manometer arms were placed outside, adjacent to each other.

Manometer readings were made with an accuracy of 0.05 mm.; using a cathetometer. The scale of this cathetometer was checked for accuracy against a high-grade, imported Swiss instrument belonging to the Physics Department of this University.

¹² Keyes, Townshend and Young, *J. Math. Phys. Mass. Inst. Techn.*, **1**, No. 4 (1922).

¹³ Cath, *Leiden Comm.*, **152d** (1918), $\log p_{O_2} = -419.3/T + 5.2365 - 0.0064 T$, where p is expressed in atmospheres.

¹⁴ Henning, *Ann. Physik*, **43**, 287 (1914). $T_{CO_2} = 194.610/[1 - (0.14428 \log p/760)]$.

¹⁵ Taylor and Smith, *This Journal*, **44**, 2450 (1922).

¹⁶ Walters and Loomis, *ibid.*, **47**, 2302 (1925).

The Pycnometer.—All density measurements were made with a pycnometer, shown in Fig. 1, of the type described by Keyes and Felsing;¹⁷ five small bulbs were blown into the capillary stem of the pycnometer, allowing six scales to be engraved and calibrated. The volume was determined for each scale by filling with pure mercury, boiling under a vacuum, cooling to 0° in a thermostat, reading the mercury level and then weighing. All weights were corrected to a vacuum. The volume of capillary per millimeter length had previously been determined. The volumes

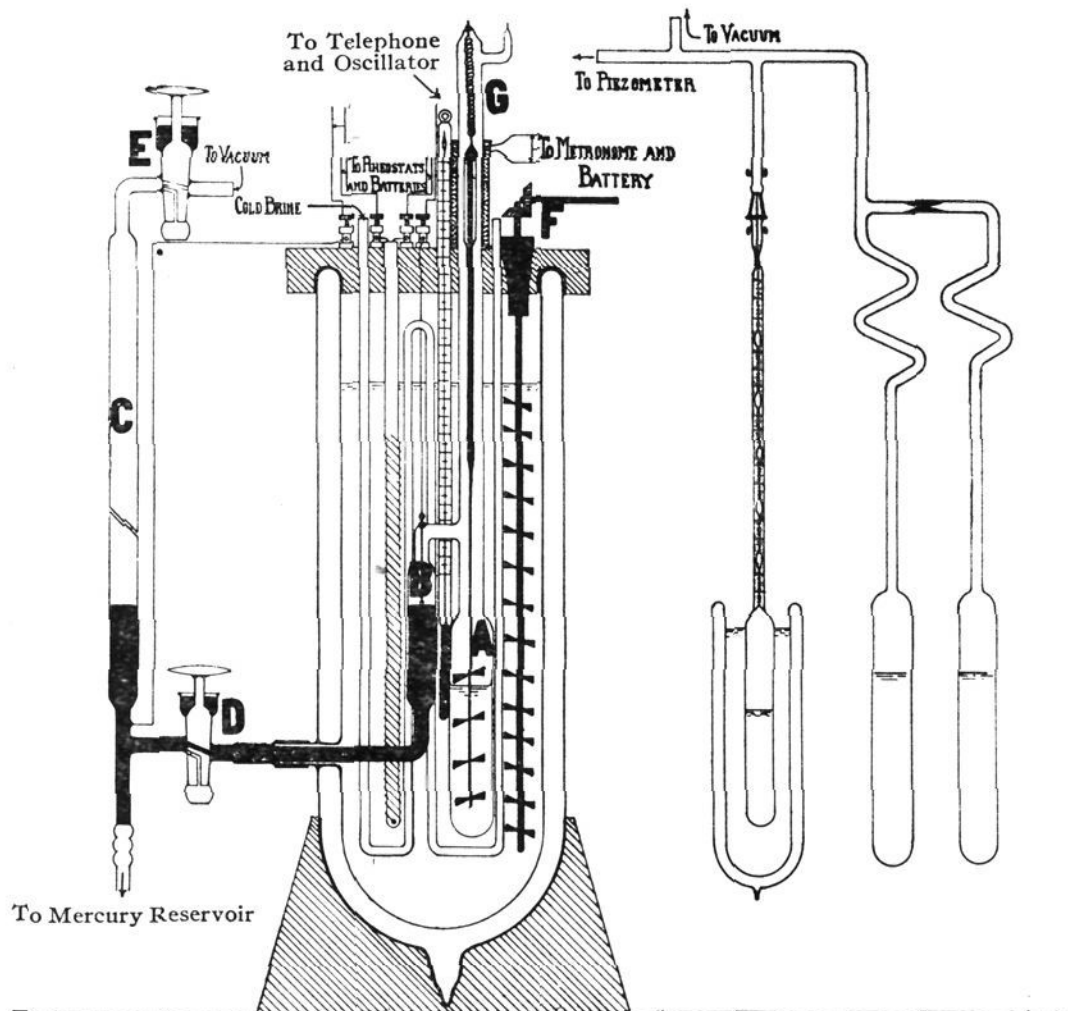


Fig. 1.

of the pycnometer itself at any temperature and scale reading were calculated from a knowledge of its volume at 0° and from the cubical coefficient of expansion of Thüringer soda glass, of which the pycnometer was constructed. The relation used was

$$V_t \text{ pycnometer} = V_0 [1 + (27.45 \times 10^{-6} + 3.57 \times 10^{-8} t) t] \quad (2)$$

The Loading Apparatus.—The acetone loaded into the pycnometer or into the piezometer was introduced in the manner shown in Fig. 1. In filling either apparatus, the crystalline acetone—sodium-iodide addi-

¹⁷ Keyes and Felsing, THIS JOURNAL, 41, 589 (1919).

tion compound was cooled by surrounding the reservoir with liquid air before evacuating the system. This evacuation was accomplished by means of two mercury-vapor pumps in series and backed by a "Hi-vac" pump. After complete evacuation, a cooling of the pycnometer or of the piezometer and a warming of the acetone—sodium-iodide reservoir provided a simple and safe transfer of the acetone.

The Preparation of Pure Acetone.—The best c. p. acetone obtainable was thrice distilled, using a Glinsky distilling column. Only the middle portion of each distillation was collected for redistillation or use. The final product was converted into the crystalline addition compound with sodium iodide, $\text{NaI} \cdot 3(\text{CH}_3)_2\text{CO}$, by treatment at room temperature with twice recrystallized, dry, finely powdered sodium iodide. The light orange crystals were separated from the mother liquor by suction filtration. These crystals were placed in a distilling flask and the acetone was distilled from them onto purified and dry sodium iodide in the receiving flask. Again the addition compound was allowed to form, the crystals were filtered off and placed in the reservoir, which in turn was sealed to the loading apparatus. After partial evacuation, the acetone addition compound was frozen by means of liquid air, and the system highly evacuated. The frozen mass was allowed to melt and it was then distilled in a vacuum into a secondary reservoir partly filled with anhydrous sodium iodide. The anhydrous sodium iodide removed the last traces of moisture that might have been left in the acetone. The first reservoir was then sealed off from the system, and the acetone distilled from the secondary reservoir into the pycnometer and the piezometer as needed.

The Experimental Data

The experimental data of this investigation include vapor pressure, density and carbon dioxide solubility measurements.

The Vapor Pressures.—The determinations were made over a range about -70° to $+65^\circ$. Several readings were made for each temperature

TABLE I
OBSERVED AND CALCULATED VAPOR PRESSURES OF ACETONE

No.	Temp., °C.	Vap. press., mm. (Obs.)	Vap. press., mm. Calcd. by (3)	No.	Temp., °C.	Vap. press., mm. (Obs.)	Vap. press., mm. Calcd. by (3)
1	-69.50	0.442	0.351	17	+2.82	82.38	82.54
2	-63.60	.708	.663	18	3.46	84.63	84.78
3	-60.70	.898	.891	19	4.08	97.61	97.45
4	-39.10	5.979	5.974	20	8.88	110.82	110.73
5	-36.11	7.474	7.507	21	9.91	116.70	116.10
6	-29.90	11.86	11.76	22	15.79	152.74	152.35
7	-23.80	17.74	17.77	23	18.34	171.64	170.72
8	-19.81	26.10	26.02	24	21.48	195.61	195.74
9	-15.90	29.20	29.22	25	26.71	244.79	244.06
10	-11.03	38.87	38.93	26	35.07	340.99	341.21
11	- 8.65	45.31	44.57	27	41.53	436.30	436.22
12	- 6.10	51.40	51.35	28	45.51	505.72	504.88
13	- 4.20	55.82	55.94	29	50.40	601.36	601.27
14	- 3.41	59.52	59.44	30	55.07	707.80	707.11
15	- 0.20	69.68	70.34	31	60.58	853.10	853.57
16	+ 0.31	72.30	72.22	32	65.80	1024.78	1025.87

point, approaching the value from both sides. The observed values are plotted on a large scale, $\log_{10} p$ against $1/T$; in order to extrapolate the resulting curve to temperatures lower than -70° , the somewhat irregular data of Drucker, Jiménez and Kangro³ were also plotted on the same graph, and their lower points used in the extension of our curve into the temperature region below our measurements and where our manometer became insensitive. The data may be expressed by the relation

$$\log_{10} p = -2986.21241/T + 20.7587806 - 40.8472641 \times 10^{-3} T + 42.6623920 \times 10^{-6} T^2 \quad (3)$$

where p is expressed in millimeters ($1/760$ of the normal atmosphere) and T in degrees K. This relation is believed to represent an accuracy of at least 0.1 mm. of mercury over the range investigated, even though a few determinations vary from the values calculated by this relation by more than that amount. The data are listed in Table I.

The Densities.—The necessary corrections for the expansion or contraction of the pycnometer itself and for the amount of acetone remaining in the vapor state were applied at each reading. The densities were recorded in grams per cubic centimeter; the observed values were plotted on large graph paper, and a curve was drawn. The relation found was

$$d(\text{g./cc.}) = 1.091301 - 92.722 \times 10^{-5} T - 32.331 \times 10^{-8} T^2 \quad (4)$$

This relation reproduces experimental values with a mean deviation of 1 part in 4000; most points are more closely reproduced. It is believed

TABLE II
THE DENSITIES AND SPECIFIC VOLUMES OF ACETONE

No.	Temp., °C.	Density by (4)	Specific vol., cc./g.	Density (Obs.)	Density from other observers
1	-90.00	0.91065	1.09811	0.91065	0.91098 ^s
2	-80.00	.90015	1.11092		.89998 ^s
3	-75.00	.89489	1.11745	.89480	
4	-70.00	.88961	1.12409		.88875 ^s
5	-60.00	.87899	1.13864		.87765 ^s
6	-56.18	.87491	1.14297	.87480	
7	-50.00	.86830	1.15167		.86787 ^s
8	-40.00	.85756	1.16610		.85748 ^s
9	-38.36	.85579	1.16851	.85588	
10	-30.00	.84675	1.18099		.84740 ^s
11	-20.00	.83587	1.19636		
12	-17.45	.83308	1.20036	.83318	
13	-10.00	.82493	1.21222		
14	- 8.40	.82328	1.21465	.82266	
15	- 6.40	.82108	1.21791	.82086	
16	- 6.00	.82053	1.21872	.82067	
17	± 0.00	.81392	1.22862	.81392	.81248 ^{1d} .81249 ^{7e} .81300 ^{11a} .81400 ^s .81460 ¹⁰

TABLE II (Concluded)

No.	Temp., °C.	Density by (4)	Specific vol., cc./g.	Density (Obs.)	Density from other observers
18	6.69	.80652	1.23990	.80716	
19	10.00	.80285	1.24550		.8030 ¹⁰
20	15.00	.79729	1.25425		.79726 ⁹ .7975 ^{11f}
21	18.00	.79395	1.25952		.7938 ^{11f} .79408 ⁹
22	18.80	.79305	1.26095	.79306	
23	20.00	.79171	1.26309		.790727 ⁹ .7908 ^{11g} .79082 ⁶ .7912 ¹⁰ .7915 ^{11h} .79197 ⁹ .7920 ^{11b}
24	22.25	.78920	1.26710	.78984	
25	25.00	.78612	1.27207		.78630 ⁹
26	30.00	.78051			.7793 ¹⁰ .77931 ⁸
27	32.84	.77732	1.28647	.77762	
28	35.88	.77390	1.29216	.77390	
29	40.00	.76925	1.28122		.7674 ¹⁰ .76784 ⁸
30	50.00	.75792	1.31940		.7555 ¹⁰ .75599 ⁶
31	51.65	.75604	1.32268	.75593	

that the relation gives true values of the density to within 1 part in 3000-4000; the data are listed in Table II.

The Solubility of Carbon Dioxide in Acetone.—The apparatus, in essential details, is shown in Fig. 2. The loading device was of the type used by Keyes and Felsing.¹⁷ All necessary corrections for the acetone vapor remaining in the loading pycnometer and for the acetone and carbon dioxide in the gaseous state above the acetone—carbon dioxide solution in the piezometer were applied as usual. Since it was desired to determine the solubility of carbon dioxide at a partial pressure equal to 760 mm., the manometer pressure (total pressure P) was so adjusted that it was equal to 760 mm. *plus* the acetone

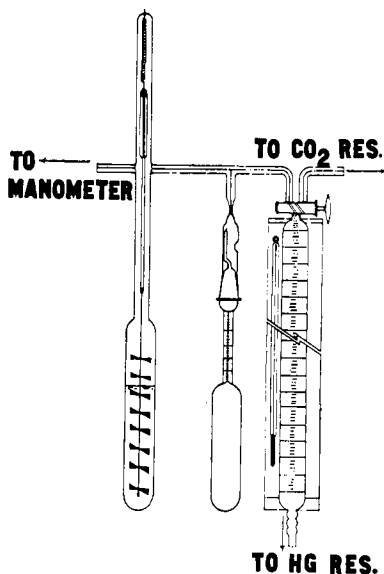


Fig. 2.

vapor pressure at the particular temperature. The solubility is expressed in moles of carbon dioxide per 1000 g. of acetone and in cubic centimeters ($0^\circ/760$ mm.) per 1000 g. of acetone. The relation between this carbon dioxide solubility and temperature is given by

$$\log_{10} S = 2615.017/T - 18.085436 + 66.55546 \times 10^{-3} T - 79.07114 \times 10^{-6} T^2 \quad (5)$$

where S is expressed in moles per 1000 g. of acetone when the partial pressure of carbon dioxide is 760 mm., and T is given in degrees K. The data are given in Table III.

TABLE III
THE SOLUBILITY OF CARBON DIOXIDE IN ACETONE

No.	Temp., °C.	Solubility, moles/1000 g.	Solubility, cc. ($0^\circ/760$)/1000 g.
1	+20.00	0.35537	7,966.2
2	- 2.54	.62115	13,924.0
3	-13.55	.90322	20,247.1
4	-29.24	1.47773	33,125.6
5	-45.14	2.79867	62,736.6
6	-60.12	5.92017	132,710.1
7	-73.14	13.94490	312,597.1

The Calculated Heats of Evaporation for Acetone

The vapor-pressure—temperature relation (Equation 3) being available, the heats of evaporation of acetone at different temperatures could be calculated by means of the familiar Clausius-Clapeyron relation

$$\Delta H_L = T(v_1 - v_2) dp/dT \quad (6)$$

where ΔH_L is the latent heat of evaporation, v_1 the molal volume of the vapor and v_2 the molal volume of the liquid acetone.

By multiplying Equation 3 by 2.3026 there follows the relation

$$\ln p = -6876.05238/T + 47.7991648 - 94.0550 \times 10^{-3} T + 98.2344318 \times 10^{-6} T^2 \quad (7)$$

which becomes, upon differentiation,

$$dp/dT = (6876.05238/T^2 - 0.094055 + 19.6468863 \times 10^{-5} T)p \quad (8)$$

In order to evaluate v_1 , the ideal gas law was used; only one datum on critical constants, by Sabjotchewsky,¹³ was available for the evaluation of the constants a and b of the van der Waals equation or for the application of Berthelot's equation for acetone. Hence, it was believed best to use the ideal gas law even at the higher pressures. Values of v_2 were calculated from the density relation (Equation 4).

The values of the latent heat of vaporization thus calculated are compared with the few experimentally determined values in Table IV; the heats are given in mean calories per gram.

¹³ Sabjotchewsky, *Beibl. Ann. Physik*, **3**, 741 (1879).

TABLE IV
THE HEATS OF EVAPORATION OF ACETONE

Temp., °C.	-60.00	-40.00	-20.00	0.00	20.00
ΔH_L calcd., cal./g.	155.46	149.68	143.92	138.05	132.14
ΔH_L observed cal./g.				140.50 ¹⁹	
				139.90 ²⁰	
Temp., °C.	40.00	55.51	56.32	56.60	60.00
ΔH_L calcd., cal./g.	126.45	121.81	121.58	121.50	120.48
ΔH_L observed, cal./g.		124.00 ²¹	125.00 ²⁰	123.30 ²²	128.80 ²³

Summary

1. The vapor pressures and densities of pure, anhydrous acetone have been measured over a large temperature range.
2. The solubility of carbon dioxide in acetone has been determined over the range $+20^\circ$ to -75° .
3. The latent heats of evaporation of acetone have been calculated by means of the Clausius-Clapeyron relation.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]
A STUDY OF NEGATIVE CATALYSIS IN THE OXIDATION OF
BENZALDEHYDE

BY ORLAND M. REIFF¹

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An explanation for the mechanism of negative catalysis in homogeneous chemical reactions has been sought in the well-known theories of Titoff,² Taylor³ and Christiansen;⁴ on the other hand, negative catalysis in heterogeneous chemical reactions has been plausibly explained by the assumption of adsorption of the inhibitor on the positive catalyst surface.

Moureu and Dufraisse⁵ have pointed out the high inhibitory power of phenolic substances in a variety of so-called auto-oxidations, such as the oxidation of benzaldehyde and acrolein and the oxidation of sodium sulfite; inhibitors added one part in one million were shown to give appreciable retardation.

In order to explain this high inhibitory power in homogeneous solution

¹⁹ Regnault, *Relat. exp. mach. feu*, **2**, 813 (1862).

²⁰ Winklemann, *Wied. Ann.*, **9**, 364 (1880).

²¹ Tyres, *J. Chem. Soc.*, **181**, 1105 (1912).

²² Wirtz, *Wied. Ann.*, **40**, 446 (1890).

²³ Young, *Dublin Proc.*, (N. S.) **12**, 374 (1910).

¹ Grafflin Scholar in Chemistry, Johns Hopkins University.

² Titoff, *Z. physik. Chem.*, **45**, 641 (1903).

³ Taylor, *J. Phys. Chem.*, **27**, 322 (1923).

⁴ Christiansen, *ibid.*, **28**, 145 (1924).

⁵ Moureu and Dufraisse, *Compt. rend.*, **174**, 258; **175**, 127 (1922).