[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 434]

THE PURIFICATION AND PHYSICAL CONSTANTS OF ACETOPHENONE

BY J. LIVINGSTON R. MORGAN AND OLIVE M. LAMMERT

RECEIVED JANUARY 7, 1924

Having occasion to use for solvent purposes a large quantity of the purest acetophenone available, we have made a search of the literature for a criterion of purity and a method of purification, but with the most discouraging result. For example, the highest value for the freezing point, and the one usually cited in compilations of physical constants, is 20.5° (probably this is from Staedel and Kleinschmidt[1] who give no further information than the statement that pure acetophenone, instead of melting at 16°, as stated in the text-books of that time, melts at 20.5°) but, whenever special attempts at purification have been made, the values given for the freezing point are usually lower.

For comparison, these and the values of other physical constants determined up to the present time are summarized in Table I.

TABLE I

PHYSICAL CONSTANTS OF ACETOPHENONE

Observer reference	M. p. °C.	B. p. °C.	D.	Sp. conductance	Other constants	Method of purification Footnote
					Dielectric constant (ε)	
9	...	.....	....	....	$\epsilon = 15.6$ (21°)	*a*
40	...	.....	$d_4^{15} = 1.032$	....	$\epsilon = 16.24$ (15°)	*a*
41	...	.....	....	....	$\epsilon = 18.6$ (20°)	*a*
42	...	.....	....	....	ε given at various temperatures	*b*
					Viscosity (η)	
4	...	.....	values at various temps.	....	$\eta_{25°} = 0.01669$	*c*
8	...	.....	$d_4^{10} = 1.0358$ $d_4^{80} = 0.9758$	....	$\eta_{10°} = 0.02270$ $\eta_{80°} = 0.00734$	*d*
11	20.5	200.9–201 (725 mm.)	temp. equation given	Viscosity and surface tension values given		*e*
18	...	202.3 ± 0.1	$d_4^{25} = 1.0263$	5.5×10^{-8} mho (25°)	$\eta_{25°} = 0.01681$	*f*
21	...	202.3 ± 0.1	....	5.5×10^{-8} mho (25°)	$\eta_{25°} = 0.01681$	*f*
22	...	.....	....	....	Relative η given	*c*
23	...	.....	$d_4^{25} = 1.0224$ $d_4^{50} = 0.9981$	....	$\eta_{25°} = 0.01617$ $\eta_{50°} = 0.01246$	*c*
33	...	.....	....	....	$\eta_{25°} = 0.01669$	*c*
35	...	.....	$d_4^{25} = 1.0252$	....	$\eta_{25°} = 0.01645$	*c*
					Index of refraction (*n*)	
3	...	.....	$d_4^{20} = 1.028$	....	$n_{\alpha}^{20} = 1.5283$ $n_{D}^{20} = 1.5339$	*a*

---

[1] Staedel and Kleinschmidt, *Ber.*, **13**, 836 (1880).

Table I (*Continued*)

Observer reference	M. p. °C.	B. p. °C.	D.	Sp. conductance	Other constants	Method of purification Footnote
6	...	201–202 (748.5 mm.)	$d_4^{19.5} = 1.0277$ $d_4^{20} = 1.0272$	....	$n_\alpha^{19.6} = 1.52876$ $n_D^{19.6} = 1.53418$	*b*
5	19.6	.....	....	....	....	*g*
7	...	.....	....	2.02×10^{-7} mho 16–17°	....	*d*
10	20	202	....	....	....	*a*
12	16–17	.....	....	....	....	*a*
19	18.7	.....	....	....	....	*a*
20	18.7	.....	....	....	....	*a*
25	...	194–195 (745 mm.)	....	1.8×10^{-7} R. S. U.	....	*h*
34	...	199–200	....	....	....	*a*
36	...	.....	....	1.6×10^{-6} R. S. U.	....	*a*
37	19.5	201.5 (760 mm.)	$d_4^{20} = 1.030$	....	....	*i*
43	20	.....	....	2×10^{-7} R. S. U.	....	*k*
16	...	201.5	values at various temps.	Surface tension values at various temps.		*c*
32	...	202 (760 mm.)	$d_4^{20} = 1.0296$ $d_4^{25} = 1.0266$	Magnetic rotatory power given		*i*
17	19.5+	201.5 (760 mm.)	....	$\frac{dp}{dt}$ values at various temperatures		*d*
26	...	203.7	....	Specific heat 0.4744, 20–96° Heat of evaporation, 77.24 cal.		*d*
39	20.6 20.9	201.4–202 (756 mm.)	....	Heats of formation and combination given		*j*
2	18	.....	Crystal structure: monoclinic a:b::1.0428:1; $\beta = 111°10''$			*a*
13	19.5	.....	....	Cryoscopic constant, $K = 5.65$		*d*
14	...	.....	....	Surface-tension values given		*a*
15	...	.....	....	Vapor-pressure equation given		*a*
24	...	.....	....	....	Kerr's constant, 2060	*a*
27	20.0	.....	....	Heat of fusion at 20°, 33.12 cal. per g.		*e*
28	19.5	.....	....	....	....	*c*
29	...	.....	Equation for surface tension and capillary constants			*a*
30	19	.....	....	Magnetic susceptibility values given		*a*
31	...	.....	Molecular susceptibility, dia- and para-magnetism values			*a*
1	20.5	.....	....	....	....	*a*
38	...	.....	....	Heats of combustion and formation given		*a*

[a] None given.

[b] Dehydrated, distilled in a vacuum.

[c] Original not consulted.

[d] Distilled and recrystallized.

[e] Recrystallized to constant melting point.

[f] Distilled from phosphorus pentoxide, atmospheric pressure.

[g] Recrystallized very slowly.

[h] Distilled from barium oxide, atmospheric pressure.

[i] Recrystallized.

[j] Distilled at atmospheric pressure.

[k] Distilled from alkali dehydrating agents, atmospheric pressure.

---

[2] Aminoff, *Arkiv. Kemi Min.*, **6,** No. 4 (1916).

[3] Auwers and Eisenlohr, *J. prakt. Chem.*, [2] **82,** 65 (1910).

[4] Bregman, *Thèse*, Lausanne, **1914.**

[5] Bridgman, *Phys. Rev.*, [2] **3,** 126 (1914); [2] **6,** 1 (1915).

[6] Brühl, *J. prakt. Chem.*, [2] **50,** 119 (1894).

[7] Creighton, *Proc. Nov. Scot. Inst.*, **13,** 154 (1912).

[8] Drucker and Kassel, *Z. physik. Chem.*, **76,** 367 (1911).

[9] Drude, *ibid.*, **23,** 267 (1897).

[10] Dunstan and Hilditch, *Z. Elektrochem.*, **18,** 185 (1912).

[11] Dutoit and Friederich, *Bull. soc. chim.*, [3] **19,** 321 (1898); *Arch. sci. phys. nat.*, [4] **9,** 105 (1900).

[12] Friedel and Balsohn, *Bull. soc. chim.*, [2] **35,** 54 (1881).

[13] Garelli and Montanari, *Gazz. chim. ital.*, [II] **24,** 229 (1894).

[14] Guye and Perrot, *Arch. sci. phys. nat.*, [4] **11,** 225 (1901).

[15] Ham, Churchill and Ryder, *J. Franklin Inst.*, **186,** 15 (1918).

[16] Jaeger and Smit, *Proc. akad. Wetenschappen Amsterdam*, **17,** 386 (1913).

[17] Kahlbaum, *Z. physik. Chem.*, **26,** 577 (1898).

[18] Kendall and Brakeley, THIS JOURNAL, **43,** 1826 (1921).

[19] Kendall and Carpenter, *ibid.*, **36,** 2498 (1914).

[20] Kendall and Gibbons, *ibid.*, **37,** 149 (1915).

[21] Kendall and Gross, *ibid.*, **43,** 1426 (1921).

[22] Kremann, Gugl and Weingast, *Monatsh.*, **35,** 1365 (1914).

[23] Kurnakow, Krotkow and Oksman, *J. Soc. Physic. Chim. St. Pet.*, **47,** 563 (1915); *Bl. Acad. Sc. Pet.*, **9,** 45 (1916).

[24] Leiser, "Elektrische Doppelbrechung der kohlenstoff Verbindungen," W. Knapp, Halle, **1910.**

[25] Lincoln, *J. Phys. Chem.*, **3,** 457 (1899); *Trans. Wisconsin Acad.*, [2] **12,** 395 (1899).

[26] Louguinine, *Arch. sci. phys. nat.*, [4] **9,** 5 (1900).

[27] Louguinine and Dupont, *Bull. soc. chim.*, [4] **9,** 223 (1911).

[28] Menshutkin, *Mem. St. Pet. Polyt. Inst.*, **15,** 65 (1911).

[29] Morgan and Stone, THIS JOURNAL, **35,** 1505 (1913).

[30] Oxley, *Phil. Trans. Roy. Soc.* (London) **214A,** 109 (1914).

[31] Pascal, *Ann. chim. phys.*, **19,** 5 (1910); *ibid.*, [8] **25,** 289 (1912).

[32] Perkin, *J. Chem. Soc.*, **69,** 1025 (1896).

[33] Polliack, *Thèse*, Lausanne, **1913.**

[34] Popoff, *Ber.*, **4,** 720 (1871).

[35] Sachanov and Rjachowski, *J. Soc. Phys. Chem. St. Pet.*, **47,** 128 (1915).

[36] Sammis, *J. Phys. Chem.*, **10,** 593 (1906).

[37] Senderens, *Compt. rend.*, **150,** 1336 (1910); *Ann. chim. phys.*, [8] **28,** 243 (1913).

[38] Stohmann, *Z. physik. Chem.*, **10,** 410 (1892).

[39] Stohmann, Rodatz and Herzberg, *J. prakt. Chem.*, [2] **36,** 357 (1887).

[40] Thwing, *Z. physik. Chem.*, **14,** 286 (1894).

[41] Turner, *ibid.*, **35,** 385 (1900).

[42] Walden, *ibid.*, **70,** 569 (1910).

[43] Nicollier, *Thèse*, Dutoit, Lausanne, **1907.**

Quite apparently, although the physical constants of acetophenone by virtue of its composition have been the subject of considerable interest in the past, there can be little certainty that in any case the pure substance has been obtained, since in general the experimental detail, either in the methods of purification, or in the methods for the determination of the constants, is too meager to be reassuring.

The usual methods of distillation from dehydrating agents result, we have found, in the decomposition of the acetophenone and the production of water. When it is distilled under reduced pressure, a larger number of distillations are needed to bring the freezing point up to 19.3° and it is almost impossible to raise it above that point. Comparable to this experience is that of Kahlbaum who obtained in a vacuum apparatus a product boiling between 201.4° and 201.7° and melting at 19.2°. It was only when the crystals from this distillate were centrifuged that the melting point rose to 19.5°, and Kahlbaum states that in all probability this melting point could be raised.

The method of purification which we have used is as follows.

The commercial sample found most satisfactory freezes at 17–18°, although we have had some samples freezing at 19.0°. This product, usually containing considerable suspended matter, is filtered through folded filters into 2 to 3-liter bottles. The liquid is subcooled somewhat and a glass rod introduced to start the crystallization. In passing, it might be mentioned that this liquid, except when contaminated with comparatively large amounts of water, exhibits to a marked degree the phenomenon of over-cooling, and it is only by the introduction of some foreign substance or a crystal that crystallization can be induced. The bottle is stoppered and the separation of the solid continued by placing the bottle in a refrigerator, preferably at a temperature not more than a degree lower than the freezing point of the liquid, until only a few cubic centimeters remain liquid. This liquid is then poured off as quickly as possible, and the solid melted until only a small crystal remains upon which the new crystals can grow. This process is continued until a product with a constant freezing point is obtained. Because of the hygroscopic nature of acetophenone, it is found necessary for the final recrystallizations to seal even the most carefully ground glass-stoppered bottles. To avoid impurities at the neck, a beaker or bottle top is placed over the top and then sealed with paraffined cloth around the shoulder of the bottle. As acetophenone is affected by oxygen in the presence of light, the bottles must be protected from the light.

After removal of the *pure* fraction, the residual fractions should be distilled once, at atmospheric pressure, through a Vigreux column, since it has been found that large quantities of water can be removed more effectively by distillation than by crystallization. The distillate is then further purified by slow crystallization; in this way almost all of the commercial product can be purified. This method was found to be effective for commercial samples from several sources.

Physical Constants of Acetophenone

Freezing Point.—The freezing point of the pure solvent was determined in a large air-jacketed tube of about 500cc. capacity. The stirrer was handled through a T-tube into which was passed dried, purified air. The usual precautions of subcooling and stirring were observed, and stem corrections made for different parts of the standard thermometers used. Between determinations, the solvent was slowly frozen three or four times in an attempt to further purify it, during which time the tube was tightly stoppered and placed in a desiccator.

The freezing points for the water-acetophenone curve were taken in the large tube. The concentrations of water and acetophenone were determined by weight, the water by difference from a weighing tube, the acetophenone by direct weighing of the freezing-point tube.

Although more than 50 liters of acetophenone from different sources have been purified in this Laboratory by two workers, in no case were we able to obtain a product with a freezing point higher than 19.655° ± 0.002° on a Bureau of Standards thermometer, No. 27627. This checked to within 0.001° a value 19.654°, found earlier on a Reichsanstalt thermometer, No. 5853. In view of the fact that Bridgman reported that he was unable to obtain a product with a freezing point of 20.5° and could not raise his value above 19.6°, and in view of the fact that most other workers who have purified by recrystallization report a value of 19.5° and it was only on the very driest of days that we were able to obtain a freezing point higher than this when recrystallizing in an open flask, it seems very probable that the value 20.5° so generally quoted and striven for is too high, and that the freezing point of pure acetophenone is close to our value, *19.655°*.

The effect of dissolved air on the freezing point, as in the case of benzene,[44] may be of interest; this has not been fixed, but it is noticeable that as the acetophenone becomes purer, less air is included between the crystals, until finally with the very pure fractions, the acetophenone freezes as a clear, glassy mass.

The previous investigators, who have reported a criterion of purity and a freezing point value *higher* than *19.655°*, are Dutoit and Friederich, and Louguinine and Dupont; in both cases they recrystallized to a constant freezing point, but in neither case did they report their thermometer precision nor make any mention of the hygroscopic nature of acetophenone; this would most certainly have been manifested with a product purer than ours. It seems likely, therefore, that these investigators were more interested in the other properties of a substance of definite purity than in the absolute value of the freezing point.

The effect of water on the freezing point is shown in Fig. 1, and the data in Table II. When the last freezing point was taken the acetophenone was supersaturated with water; the point at which the continuation of the curve crosses the axis representing the freezing point of the saturated mixture probably gives very nearly the maximum solubility of water in acetophenone.

---

[44] Richards, Carver and Schumb, THIS JOURNAL, **41,** 2019 (1919).

TABLE II

EXPERIMENTAL AND CALCULATED DATA FOR FREEZING-POINT CURVES OF WATER-ACETOPHENONE MIXTURES (FIGS. 1 AND 2)

G. of H_2O per 1000 g. of $C_6H_5COCH_3$

H_2O G.	Beckmann degrees	Standard °C.	Mole fraction $C_6H_5COCH_3$ (X)	log X	$I/T \times 10^3$
0	3.867	19.655	1.000	0	3.4170
0.5741	3.680	19.468	0.9962	$\bar{1}$.9984	3.4192
1.2449	3.439	19.227	.9918	.9964	3.4220
1.938	3.250	19.038	.9873	.9944	3.4242
2.644	3.079	18.867	.9827	.9924	3.4262
3.228	2.948	18.736	.9789	.9907	3.4278
3.848	2.798	18.586	.9750	.9890	3.4295
5.026	2.557	18.345	.9676	.9857	3.4324
9.932	1.685	17.473	.9379	.9721	3.4427
13.285	1.175	16.963	.9186	.9631	3.4487
19.382	0.551	16.339	.8856	.9472	3.4562

In the last three columns of this table are given the calculated data necessary for plotting the general freezing-point law,[45] $R\ ln\ X = \frac{-L_{F0}\Delta t_F}{F_0 F}$ from which the graph shown in Fig. 2 is constructed. This shows the deviation of the system of water in acetophenone from the law, a plot of which would result in a straight line were the log of the mole fraction of the acetophenone plotted against the reciprocal of the absolute temperature of the freezing point of the solution. Apparently, then, the freezing-point law does not hold for water dissolved in acetophenone.

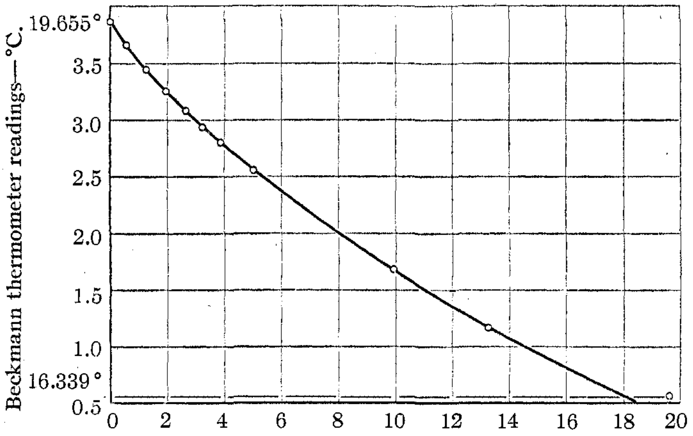

Fig. 1.

Electrical Conductance.—The average of a number of values for the specific conductance of acetophenone gave the value 6.43×10^{-9} reciprocal

---

[45] Washburn, "Principles of Physical Chemistry," McGraw-Hill Book Co., 1915.

ohm at 25° ± 0.002°, although some values as low as 6.12×10^{-4} were obtained. The same bridge assembly and precautions in cleansing and drying of the cells as discussed in a previous paper were used.[46]

Inasmuch as, at the present writing, we have found no satisfactory cell which with a liquid having such a high specific resistance would give a reading in the middle of the bridge, this value is burdened with the error due to the reading being taken near one end. Measurements made in some cells nearer the center of the bridge gave values of the same order; the more apparent errors inherent in the construction of those cells and the fact that a greater precision if not accuracy could be obtained with the Washburn Type A cell used, made it seem advisable to report the value found in that cell rather than to complicate it further by additional cell-constant determinations.

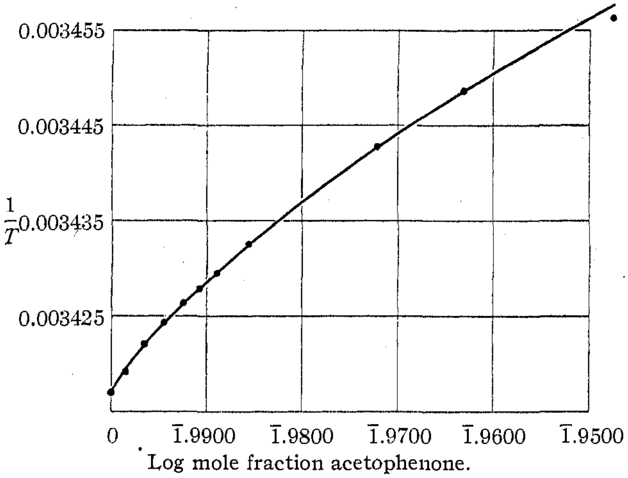

Fig. 2.

For the purer fractions, then, if water is the only impurity, either the freezing point or the conductance values will give a criterion of the purity of a sample of acetophenone. However, if the sample has been exposed to light the conductance is much more affected than the freezing-point value. A sample which had been exposed to the light long enough to change the specific conductance from 6.43×10^{-9} to 1.28×10^{-7} reciprocal ohm had a freezing point as high as 19.643°. On the other hand, a sample which has been exposed to the light and then placed in the dark, *decreases* in conductance while the freezing point continues to decrease; such a change is accompanied by a change in color, the colorless becoming more or less yellow, depending upon the time of the previous exposure to the

---

[46] Morgan and Lammert, This Journal, **45**, 1692 (1923).

light. The history, then, is of importance as well as the constants in judging the purity of acetophenone.

Density.—The density of the pure solvent at 25°, determined with a pycnometer (with the usual corrections for reducing the values to the vacuum basis, the apparent weight of 1 cc. of water being taken as 1.00400 g.), compared to water at 4° was found to be 1.02382 ± 0.002%. This agrees exactly, to the limit of their experimental error, with the value calculated from the interpolation equation of Dutoit and Friederich: $d_t = 1.0267 - 0.0_38467\ (t - 21.6) - 0.0_6596\ (t - 21.6)^2$; or $d^{25°}_{4°} = 1.0238$. It will be remembered that these authors recrystallized their acetophenone to a constant freezing point differing from ours. The impurity left, for the most part, would be water, which would have little effect on their values since it was found to have very little on ours, although ours were carried out to another decimal place. To be of value as a criterion of purity, the densities would have to be determined far more precisely than ours, but as we were interested in the density in our work only as a means of changing weight-normal concentrations to volume-normal, more accurate determinations were not made.

Summary

A large quantity of acetophenone has been purified by a method involving the slow recrystallization of the substance in the dark and in the absence of moisture, and the following constants have been determined: freezing point = 19.655° ± 0.002°; specific conductance, at 25° = 6.43×10^{-9} mho; density at 25° compared to water at 4° = 1.02382 ± 0.002%.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

EQUILIBRIA INVOLVING THE OXIDES OF IRON

BY E. D. EASTMAN AND R. M. EVANS

RECEIVED JANUARY 14, 1924

In a previous paper[1] various uncertainties in the existing data relating to the systems, iron:hydrogen:oxygen and iron:carbon:oxygen, have been pointed out and fully discussed. The work described in the present paper was undertaken in order to remove some of the more important of the uncertainties concerning the equilibria expressed by the following equations.

$$FeO + H_2 = Fe + H_2O; \quad K_1 = (H_2O)/(H_2) \qquad (1)$$
$$Fe_3O_4 + H_2 = 3FeO + H_2O; \quad K_2 = (H_2O)/(H_2) \qquad (2)$$
$$FeO + CO = Fe + CO_2; \quad K_3 = (CO_2)/(CO) \qquad (3)$$
$$Fe_3O_4 + CO = 3FeO + CO_2; \quad K_4 = (CO_2)/(CO) \qquad (4)$$

In particular it was our purpose (1) to investigate the nature of the solid phases in the iron:hydrogen:oxygen system; (2) to measure the equilib-

---

[1] Eastman, THIS JOURNAL, **44**, 975 (1922).