[CONTRIBUTION FROM THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

VARIATION WITH PRESSURE OF THE BOILING POINTS OF NAPHTHALENE, BENZOPHENONE AND ANTHRACENE[1]

BY J. L. FINCK AND R. M. WILHELM

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Introduction

The boiling points of naphthalene and benzophenone have become established as two secondary fixed points of the thermometric scale on account of their reproducibility and constancy, and the ease of manipulation. Anthracene has not been so commonly used. The only available data for calculating the variation of boiling point with pressure for naphthalene and benzophenone appear to be those due to Crafts[2] and Jaquerod and Wassmer.[3] Determinations of the boiling point of anthracene at a single pressure, within the barometric range, have been made both by Crafts[4] and by Schweitzer.[5] However, there are no data on the variation of the boiling point with pressure. Crafts' work was carried out both with mercury-in-glass and nitrogen-gas thermometers, while Schweitzer used a mercury-in-glass thermometer in which nitrogen gas was introduced over the mercury column. The developments in the platinum-resistance thermometer have proved it to be an instrument of higher precision and much higher sensitivity than any of those employed by the above-mentioned investigators, and it is at present accepted as the standard instrument for precise thermometry. It therefore seemed desirable to make a redetermination of the variation of boiling point with pressure over the range of pressures usually met under ordinary barometric conditions. With the apparatus used it was convenient to cover the range from 700 to 800 mm. of mercury. The experimental work was performed during March, 1917, but on account of the abnormal conditions then arising its publication was delayed.

Materials and Apparatus

The naphthalene used was that distributed by the Bureau as a standard material for calibration of bomb calorimeters.[6] The benzophenone was Kahlbaum "gereinigt." Two purified samples of anthracene were used, but as their normal boiling points differed by about 0.5°, the results are of value only for determining the variation of boiling point with pressure, but do not serve to establish the boiling point of anthracene as a precise fixed point in thermometry.

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[1] Published by permission of the Director, Bureau of Standards, U. S. Department of Commerce.

[2] Crafts, *Bull. soc. chim.*, **39**, 196, 277 (1883); *J. chim. phys.*, **11**, 429 (1913).

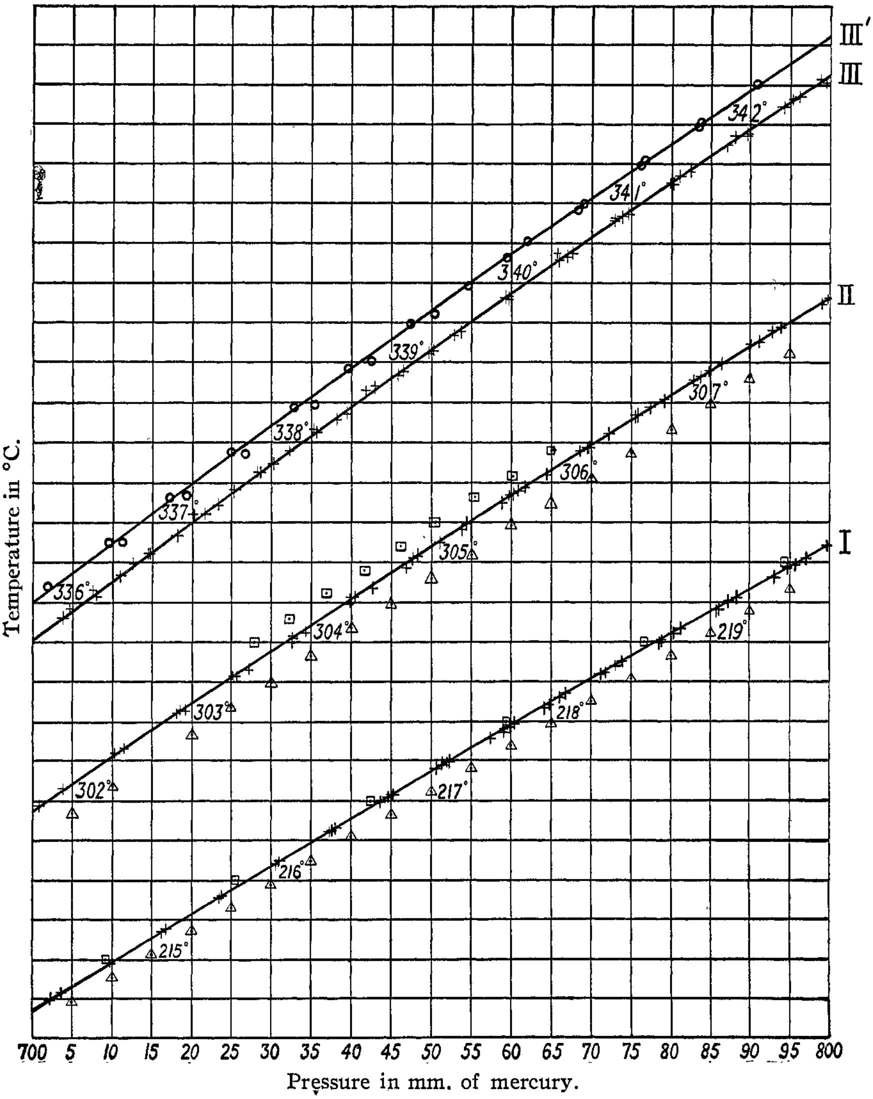
[3] Jaquerod and Wassmer, *Ber.*, **37**, 2531 (1904).

[4] Crafts, *Ann. chim. phys.*, [5] **14**, 409 (1878).

[5] Schweitzer, *Ann.*, **263**, 194 (1891).

[6] *Bur. Standards Circ.*, No. 11, 3rd ed., **1917.**

The measurements were made with the apparatus previously used by Mueller and H. A. Burgess[7] for the determinations at the boiling point of sulfur. The parts of this



Curve I from equation for naphthalene; Curve II from equation for benzophenone; Curve III from equation for anthracene ($t_{760} = 339.87°$); Curve III′ from equation for anthracene ($t_{760} = 340.36°$). + And ⊙ represent the observations by the authors on the respective substances; ⊡ observations by Crafts; △ observations by Jaquerod and Wassmer.

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[7] Mueller and Burgess, *Bur. Standards Sci. Paper*, **15**, 162; *Sci. Paper*, No. 339 (**1919**); THIS JOURNAL, **41**, 745 (1919).

apparatus comprised a glass tube, 5 cm. in diameter and 45 cm. long, in which the material was boiled, the heat being supplied electrically, and a water-sealed gasometer connected to the tube through a trap. By means of weights the gasometer could be loaded to maintain a pressure differing from that of the atmosphere by amounts up to the equivalent of 5 cm. of mercury, so that any pressure in the range from 700 to 800 mm. of mercury could be maintained. A water manometer served for measuring the difference between atmospheric pressure and that in the system. A Fuess barometer was used for measuring the atmospheric pressure. The temperature of the condensing vapor was measured with a resistance thermometer. The thermometer coil was shielded from radiation by an aluminum shield of a type previously found to be adequate.

The thermometer used was designated C_{21} and had the following constants: $R_0 = 25.5426$ ohms; $F = 9.9960$ ohms; $\delta = 1.493$. R_0 is the resistance at 0°, F the change in resistance due to heating from 0° to 100°, and δ the constant determined from observations at the boiling point of sulfur (444.6° at 760 mm.) by means of Callendar's equation,

$$t = \frac{R - R_0}{F} 100 + \delta \left(\frac{t}{100} - 1\right) \frac{t}{100}$$

where R is the resistance at a given temperature t.

Results

The observations were made, beginning at or near atmospheric pressure, then changing the pressure by steps of about 7 mm. of mercury until the lowest (or highest) pressure was reached, after which the steps were retraced in reverse order. Pressures were read and recorded to 0.01 mm. of mercury, temperatures to 0.001°.

For reducing the observations the familiar equation for vapor pressure versus temperature, $\log p = a - (b/(t + 273.1))$, was used in the form, $t_p = t_{760} + A\ (t_p + 273.1) \log (p/760)$, in which t_p represents the temperature corresponding to the pressure p, expressed in mm. of mercury; t_{760} the normal boiling point; and A a constant characteristic of the substance. Normal pressure is that due to a column of mercury at 0°, 760 mm. high, at a place where $g = 980.665$ cm. per sec.[2]

The following values of A and t_{760} were found to represent the observations best.

	t_{760}	A
Naphthalene	217.95°	0.2075
Benzophenone	305.84	.194
Anthracene	340.36 339.87	.201

In the case of anthracene the value 340.36° was obtained with the Kahlbaum sample, while the lower value, 339.87°, was obtained with the second sample.

In the following tables are given the observed data together with the values of t_p computed from the formula for naphthalene and benzophenone. The deviations Δ indicate the difference between the observed and computed temperatures. In the accompanying figure are given the

TABLE I

COMPLETE DATA ON NAPHTHALENE

p	t_p obs.	t_p calcd.	Δ	p	t_p obs.	t_p calcd.	Δ
760.21	217.966	217.952	+0.014	759.29	217.904	217.909	−0.005
766.70	218.345	218.339	+ .006	752.20	217.489	217.494	− .005
773.77	218.749	218.744	+ .005	745.02	217.071	217.070	+ .001
781.05	219.167	219.160	+ .007	737.94	216.648	216.651	− .003
788.17	219.567	219.556	+ .011	730.89	216.224	216.227	− .003
795.37	219.971	219.967	+ .004	723.76	215.799	215.799	.000
799.44	220.201	220.193	+ .008	716.74	215.382	215.369	+ .013
794.47	219.920	219.921	− .001	709.82	214.942	214.942	.000
787.08	219.506	219.494	+ .012	702.43	214.498	214.483	+ .015
780.13	219.108	219.109	− .001	699.26	214.361	214.292	+ .069
772.97	218.703	218.700	+ .003	702.38	214.487	214.482	+ .005
765.98	218.295	218.287	+ .008	709.31	214.914	214.916	− .002
758.81	217.883	217.880	+ .003	716.42	215.347	215.351	− .004
751.87	217.482	217.474	+ .008	723.56	215.785	215.790	− .005
745.01	217.073	217.070	+ .003	730.51	216.202	216.206	− .004
737.88	216.650	216.645	+ .005	737.47	216.617	216.624	− .007
730.80	216.227	216.225	+ .002	743.51	216.980	216.980	.000
723.62	215.793	215.791	+ .002	750.57	217.389	217.397	− .008
716.48	215.363	215.352	+ .011	758.92	217.873	217.887	− .014
709.31	214.914	214.913	+ .001	764.75	218.213	218.215	− .002
703.68	214.573	214.564	+ .009	771.72	218.614	218.628	− .014
709.54	214.918	214.933	− .015	778.75	219.019	219.029	− .010
716.33	215.352	215.351	+ .001	785.82	219.418	219.424	− .006
723.50	215.783	215.780	+ .003	792.80	219.816	219.825	− .009
730.54	216.204	216.208	− .004	796.97	220.052	220.060	− .008
737.34	216.620	216.616	+ .004	792.79	219.819	219.825	− .006
744.42	217.034	217.038	− .004	785.65	219.419	219.415	+ .004
751.35	217.449	217.444	+ .005	778.57	219.011	219.019	− .008
759.69	217.930	217.932	− .002	771.08	218.586	218.592	− .006
				764.02	218.172	218.183	− .011
				757.32	217.785	217.792	− .007

pressure-temperature curves for all three substances, based on the equation, while the observed data are represented by the crosses (circles for III′). The points represented by the squares are based on Crafts' data, and those represented by the triangles on Jaquerod and Wassmer's data.

The naphthalene used was of very high purity, and the observations are consistent with a simple equation to the extent which might be expected from the accuracy with which pressure and temperature were determined. The value of A obtained from these observations gives the change in boiling point in the pressure interval (700–800 mm.) with a probable accuracy of 0.01°. The temperature 217.95° found for the normal boiling point is within a few hundredths of a degree of the most reliable results of others.

The results obtained with benzophenone and anthracene are less consistent among themselves, but the series of observations are not extensive

Table II

Complete Data on Benzophenone

p	t_p obs.	t_p calcd.	Δ	p	t_p obs.	t_p calcd.	Δ
759.71	305.819	305.820	−0.001	758.76	305.741	305.762	−0.021
764.28	306.112	306.113	− .001	753.68	305.396	305.434	− .038
772.13	306.607	306.616	− .009	746.71	304.931	304.979	− .048
779.02	307.042	307.048	− .006	739.60	304.482	304.518	− .036
786.30	307.503	307.501	+ .002	732.43	304.003	304.039	− .036
793.64	307.957	307.962	− .005	725.59	303.610	303.590	+ .020
798.69	308.263	308.274	− .011	718.53	303.142	303.119	+ .023
790.84	307.780	307.787	− .007	711.50	302.650	302.640	+ .010
783.65	307.338	307.339	− .001	703.92	302.143	302.120	+ .023
775.76	306.846	306.843	+ .003	700.94	301.939	301.922	+ .017
769.47	307.447	306.449	− .002	710.18	302.583	302.542	+ .041
761.57	305.942	305.942	.000	718.08	303.100	303.080	+ .020
760.13	305.850	305.923	− .073	725.02	303.560	303.548	+ .012
754.34	305.481	305.478	+ .003	732.65	304.074	304.057	+ .017
748.12	305.067	305.071	− .004	739.78	304.538	304.530	+ .008
740.40	304.550	304.569	− .019	747.58	305.046	305.043	+ .003
732.52	304.054	304.051	+ .003	760.13	305.863	305.850	+ .013
727.12	303.640	303.688	− .048	769.65	306.461	306.454	+ .007
719.20	303.129	303.160	− .031	777.38	306.949	306.949	.000
725.08	303.560	303.556	+ .004	784.70	307.417	307.402	+ .015
734.14	304.125	304.155	− .030	792.58	307.906	307.782	+ .124
742.58	304.683	304.713	− .030	799.52	308.336	308.322	+ .014
750.97	305.236	305.257	− .021	789.89	307.746	307.730	+ .016
760.20	305.854	305.827	+ .027	782.79	307.302	307.287	+ .015
				775.58	306.851	306.832	+ .019
				768.54	306.402	306.385	+ .017
				760.74	305.897	305.876	+ .021

enough to demonstrate whether the less precise results are due to impurities in the material or to other causes. The value of the constant *A* for benzophenone and anthracene is not determined by these observations to the same accuracy as in the case of naphthalene. The number of observations is sufficient, however, to determine the value of *A* to an accuracy such that the repetition of the experimental work appeared unnecessary, since the values of *A* obtained give the change in boiling point over the pressure interval (700–800 mm.) with a probable accuracy of 0.03° for benzophenone and 0.05° for anthracene.

The temperature 305.84° found for the normal boiling point of benzophenone is very near the generally accepted value of 305.9°, and since so little was known as to the purity of the specimen, the agreement is very satisfactory. In the case of anthracene, Schweitzer's value for the normal boiling point is 351°. A review of the account of his work, however, indicates that this value need be given but little weight. A provisional value for anthracene may be given as 340°, which is in fair agreement with both Crafts' and the writers' values.

For reference, the following equation for the vapor pressure of sulfur versus temperature is given here: $t_p = 444.6 + 0.221_5 (t_p + 273.1) \log (p/760)$. This equation was deduced from the observations of Mueller and Burgess.

Summary

Data are presented on the variation with pressure of the boiling points of naphthalene and benzophenone within the pressure range of 700 to 800 mm. of mercury. The data are primarily intended for use in thermometry. The pressure-temperature relation for anthracene is also given but the normal boiling point of the pure material has not been determined with sufficient accuracy to establish it as a fixed point in precise thermometry.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORY OF COLLOID CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE USE OF SCATTERED LIGHT IN THE DETERMINATION OF THE DISTRIBUTION OF SIZE OF PARTICLES IN EMULSIONS[1]

BY ALFRED J. STAMM AND THE SVEDBERG

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The determination of the distribution of size of particles in a disperse system has been made with the application of Stokes' law by two general methods. One consists in following the rate of sedimentation of the disperse phase of a system passing a definite boundary, or settling onto a balance pan.[2] The other consists in determining the variation in the concentration of the disperse phase with height, after a definite interval of time has elapsed for sedimentation. In this method the concentrations at different heights may be determined photometrically by the variation with height in the light absorption,[2e,3] or by the intensity of the scattered light at right angles to the source. In this investigation the use of scattered light has been developed.

Inasmuch as the disperse phases used were all lighter than the dispersion medium, the direction of sedimentation of the particles was upwards. After a period of sedimentation both the concentration and the size of the particles increased progressively from the bottom to the top of the system.

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[1] A portion of a thesis submitted by Alfred J. Stamm in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[2] (a) Odén, *Proc. Roy. Soc. Edinburgh,* **36,** 219 (1916). (b) Fisher and Odén, *ibid.,* **44,** 98 (1923). (c) Odén, *Bull. Geol. Inst. Upsala,* **16** (1916). (d) Wiegner, *Landw. Vers. Sta.,* **91,** 41 (1919). (e) Svedberg and Rinde, THIS JOURNAL, **45,** 943 (1923). (f) Kraemer and Stamm, *ibid.,* **46,** 2709 (1924). (g) Kelly, *Ind. Eng. Chem.,* **16,** 928 (1924).

[3] (a) Svedberg and Nichols, THIS JOURNAL, **45,** 1910 (1923). (b) Svedberg and Rinde, *ibid.,* **46,** 2677 (1924).