All weighings were made by the method of substitution, the tare flask being of quartz and differing in weight from the reaction flask by only a few milligrams. Weighings were made on a balance sensitive to 0.01 mg. with weights which had been carefully standardized and were corrected to the vacuum standard. Electrostatic charges were eliminated by means of thorium oxide in the balance case.

The following densities were used: europium chloride, 4.47; silver, 10.49; platinum weights, 21.5. The atomic weight of silver was taken as 107.88 and that of chlorine as 35.457. The determination of the density of europium chloride is described in a later part of this paper.

II. The Specific Gravity of Europium Chloride

For the purpose of finding the buoyant effect of the air on anhydrous europium chloride in the preceding investigation, a knowledge of the density of this salt was necessary. Since the density of the anhydrous europium chloride is not given in the literature, it was determined by displacement of xylene.

Xylene was fractionally distilled, with rejection of the first and last third of the distillate, although the boiling point was constant within a degree and no solid material was left on evaporation. The specific gravity of the xylene at 35° referred to water at 4° was determined with an Ostwald pycnometer to be 0.8458.

Europium chloride was dehydrated and fused as described in the preceding part of this paper, and was weighed in the pycnometer. The salt was then quickly covered with xylene and placed in a vacuum desiccator in which the pressure was reduced until the xylene boiled gently. As soon as the air had thus been expelled from the salt, the pycnometer was filled with xylene at 35° and carefully weighed, the final weight being the mean of three trials. From the weight of the pycnometer filled with xylene and containing the salt, and the weight similarly determined without the salt, the xylene displaced was found. In Table II are shown the weight of anhydrous chloride, the weight of xylene displaced and the calculated density of anhydrous europium chloride at 35°.

TABLE II

THE DENSITY OF ANHYDROUS EUROPIUM CHLORIDE

Density of xylene d_4^{35} 0.8458

Detn.	$EuCl_3$, g.	Xylene, g.	Density of $EuCl_3$ at 35°/4°
1	0.7142	0.1351	4.472
2	.3111	.0589	4.468
3	.2747	.0520	4.469
4	.1344	.0254	4.476
		Average	4.471

Summary

1. The preparation of anhydrous europium chloride is described.

2. The ratio of europium chloride to silver is found to yield 152.30 with a mean deviation of ±0.018 as the atomic weight of europium. This value is higher by 0.3 unit than the present value assigned to europium.

3. The specific gravity of anhydrous europium chloride at 35° is found by displacement of xylene to be 4.471.

URBANA, ILL. RECEIVED JULY 2, 1934

The Purification and Physical Properties of Organic Compounds. VII. The Effect of Impurities on the Apparent Heat of Fusion

BY EVALD L. SKAU[1]

In usual practice the heat of fusion is not measured directly but is obtained graphically by plotting the heat contents for the solid and for the liquid at various temperatures, extrapolating each to the freezing point, and then finding the difference in their heat contents at that temperature. As was pointed out by Tammann,[2] the heat of fusion so determined is considerably lower if impurities are present in the sample, since the melting then takes place over a temperature range instead of at constant temperature. The heat content for the solid is thus higher than that for the pure substance at all temperatures above the melting point of the eutectic formed between the substance and the impurities, and becomes more and more markedly so as the freezing point is approached. The heat content of the liquid state is on the other hand relatively unaffected by a

---

[1] Guggenheim Fellow. Bayerische Akademie der Wissenschaften. Munich. Chemisches Institut der Universität. Frankfurt am Main. and Bureau International des Étalons Physico-chimiques. Brussels.

[2] Tammann. "Krystallisieren und Schmelzen." Leipzig. 1903. p. 14.

small amount of impurity. Bogojawlenski[3] proved experimentally that certain heats of fusion reported in the literature were too low because of the use of insufficiently pure samples in the measurements. It was later pointed out[4] that it probably is not practicable to purify a compound sufficiently to eliminate *entirely* this abnormality in the heat content of the solid caused by premature melting.

In a previous communication[5] the magnitude of the effect of definite amounts of an ideal impurity (naphthalene) on the heat content of benzene has been calculated on the assumption that the system obeys the ideal freezing point law and that no eutectic forms within the temperature range considered. The curves representing these data (see Fig. 1) have been used here to study the magnitude of the effect of impurity on the apparent heat of fusion and especially the extent to which these errors due to impurity may be eliminated by the now commonly accepted method of neglecting the heat content values for the solid just below the freezing point.

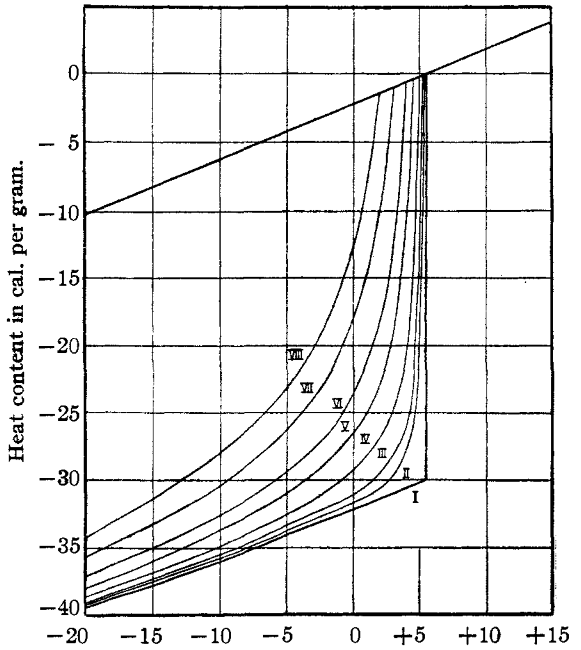

Fig. 1.—Heat content–temperature curves for benzene samples of various degrees of purity: I (the heavy curves), pure benzene, solid, liquid and supercooled liquid, f. p. 5.5°; II, f. p. 5.4°; III, 5.3°; IV, 5.0°; V, 4.5°; VI, 4.0°; VII, 3.0°; VIII, 2.0°.

Method

The heat content of the solid phase at the freezing point, t_F, of each sample, respectively, was estimated graphically by laying tangents on its heat content curve at various distances below t_F and reading the intercept of each tangent on the t_F coördinate for the sample in question. The difference between this value and the value for the heat content of the liquid at the same temperature was taken as the apparent heat of fusion. In other words, the extrapolation of the heat content curve from any temperature Δt degrees below the freezing point of the sample was assumed to be along a straight line, the tangent to the curve at this temperature, and this was considered equivalent to neglecting the heat content values for the solid for the range between this temperature and the freezing point. Actually the values of the heat of fusion so obtained are in general slightly larger than those found by the usual extrapolation along a curve slightly concave upward. The tangent is here used in the extrapolation since it can be applied much more easily and reproducibly; furthermore, since the values so obtained are all a little higher than by the usual method, the effects of the impurities can be said to be at least as great as here shown.[6]

Results

Table I gives the smoothed values for the heats of fusion so determined for pure benzene (sample I) and for a number of samples (II to VIII) containing various amounts of impurities; the freezing point t_F, and the mole fraction of impurity present, α, for each sample are listed at the top of the respective columns. Δt is $t_F - t$, where t is the temperature for which the tangent was taken, that is Δt represents the temperature range through which the heat content data for the solid state was extrapolated. Thus, for example, in the case of a sample whose freezing point is only 2.5° too low (sample VII), if all the values for the heat content of the solid within 20° of the freezing point are neglected, that is, the points lying between −17.0 and +3.0°, the

---

[3] Bogojawlenski, *Schriften Naturforsch. Gesellschaft bei der Universität Jurjeff (Dorpat)*, **13**, 1 (1904): *Chem. Zentr.*, **76**, II, 945 (1905).

[4] Dickinson and Osborne. *Bur. Standards Sci. Papers*, No. 248; *Soc. Refrigerating Engrs.*, **1**, 32 (1915); *J. Franklin Inst.*, **179**, 489 (1915). See also Smith. *Phys. Rev.*. i, **17**, 193 (1903).

[5] Skau. Paper III of this series. *J. Chem. Phys.*, **31**, 366 (1934). For a discussion of the magnitude of the specific heat and heat content as criteria of purity see also Paper V, *Bull. soc. chim. Belg.*, **43**, 287 (1934), and Paper VI. *J. Phys. Chem.*. April (1934).

[6] Only in case the extrapolations were made by the crude method of drawing a straight line through two points on the heat content curve for the solid would the apparent effect of impurities be less than here claimed.

TABLE I

APPARENT HEATS OF FUSION IN CAL./GRAM OF PURE AND IMPURE BENZENE SAMPLES

True heat of fusion of benzene, 30.09 cal./g.

	No.	I	II	III	IV	V	VI	VII	VIII
	t_F, °C.	5.5°	5.4	5.3	5.0	4.5	4.0	3.0	2.0
Δt, °C.	α	0.000	0.0015	0.0031	0.0076	0.0148	0.0227	0.0376	0.0524
1.0		30.10	21.5	19	14	8	5		
3.0		30.14	28.30	26.35	22.30	17.10	13.10	9.30	6.5
6.0		30.20	29.10	28.15	25.40	22.30	18.80	15.05	11.65
9.0		30.27	29.55	28.90	26.95	24.70	21.85	18.45	15.10
12.0		30.34	29.80	29.30	27.85	26.00	23.80	20.60	17.55
16.0		30.42	30.05	29.65	28.45	27.05	25.10	22.30	19.50
20.0		30.50	30.20	29.80	28.90	27.60	25.80	23.10	20.40
25.0		30.60	30.30	29.95	29.15	27.90	26.20	23.50	21.00

heat of fusion found is only 23.10 calories per gram.

Using 30.09 calories per gram as the correct heat of fusion the percentage errors in the various values in Table I have been calculated and these are represented graphically in Fig. 2. The following facts should be noted.

(1) *For pure benzene* the percentage error when $\Delta t = 0°$ should be zero. When the heat of fusion is gotten by extrapolating from below the freezing point, the value so obtained increases steadily with the range of extrapolation so that for $\Delta t = 25°$ it is 0.51 calorie per gram, 1.7% too *high*. Even a small amount of impurity more than counterbalances this effect, however. In the case of Sample II, for example, where the freezing point is only 0.1° too low, this positive error is exactly counterbalanced by the negative error due to the impurity when $\Delta t = 17°$, so that the correct heat of fusion is found by extrapolation of the heat content curve of the solid from this point; for smaller values of Δt the heat of fusion so measured is too low and for higher values it is too high. An amount of impurity corresponding to a freezing point lowering of only 0.2° is sufficient to cause a negative error throughout the range here considered.

(2) *For all impure samples* on the other hand the percentage error should be 100% when $\Delta t = 0$. This is obvious directly from the heat content curves. As Δt increases, the percentage error decreases very rapidly at first and then more slowly so that at large values of Δt a nearly constant though slowly decreasing value of the percentage error is obtained.

(3) The purer the sample the more rapid is this initial decrease in percentage error to the nearly constant value and the smaller and the more nearly constant is this nearly constant value.

(4) This effect of impurity on the apparent heat of fusion is enormous even though the values of the heat content of the solid near the freezing point are neglected. If, for example, the points within 5, 15 and 25°, respectively, of the freezing point are neglected, the errors due to enough impurity to lower the freezing point but 0.2° are 4.0, 1.7 and 0.5%, respectively. The corresponding series of values for a sample whose freezing point is 0.5° too low is 18.1, 5.8 and 3.2%; for 1.5°, 42.0, 17.3 and 12.9%; and for 3.5°, 66.0, 36.5 and 30.2%.

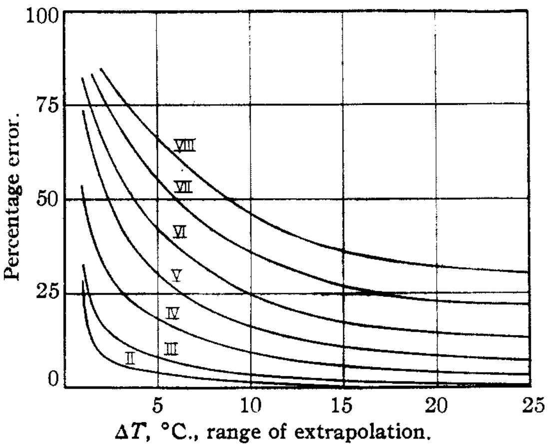

Fig. 2.—Percentage error in apparent heat of fusion by extrapolation from different distances below the freezing point for samples of benzene of various degrees of purity: II, f. p. 5.4°; III, 5.3°; IV, 5.0°; V, 4.5°; VI, 4.0°; VII, 3.0°; VIII, 2.0°; f. p. of pure benzene. 5.5°.

In ordinary practice the value of Δt is usually not greater than 10 to 15°. Thus, it is obvious from the above results that the error in the heat of fusion due to a small amount of impurity is quite considerable. Moreover, as can be seen from Fig. 2, neglecting the points over a range of even 25° or more just below the freezing point still fails to eliminate the error. Since it is often tacitly assumed that this method of correction is adequate there has probably been a tendency to be satisfied with rather impure samples for heat of fusion determinations and it therefore seems important to point out its inadequacy and the consequent necessity for the use of highly pure samples in these measurements.

Summary

The magnitude of the errors in heat of fusion determinations due to the presence of impurities in the sample, have been calculated and it has been shown that the usual method for correcting for the effects of impurity in such data, namely, by neglecting the points on the heat content curve for the solid phase near the melting point, is quite inadequate and may lead to enormous errors.

INTERNATIONAL BUREAU OF
PHYSICO-CHEMICAL STANDARDS
BRUSSELS, BELGIUM, AND
TRINITY COLLEGE
HARTFORD, CONN.

RECEIVED JULY 18, 1934

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 41]

Reaction of Fluorine with Water and with Hydroxides

BY GEORGE HAMILTON CADY

This research is the direct result of a suggestion by Professor J. H. Hildebrand, of the University of California, that at low temperatures fluorine might be absorbed by ice or a solid hydroxide, due to the formation of an oxyacid or its salts. In 1929, he and the author allowed fluorine, contained in a closed system, to react with several different solids at a temperature somewhat above that of subliming carbon dioxide. In no case did the gas pressure, during the reaction, fall below half of its initial value. Since the formation of oxygen or oxygen fluoride, OF_2, would have just halved the pressure, and since both of these gases were produced, it appeared that there was no reason for concluding that a non-volatile salt of an oxyacid of fluorine had been formed.

The investigation was continued, and the experiments to be described were carried out at the Massachusetts Institute of Technology.

I. Reactions with Solid Hydroxides

From Moissan,[1] one learns that fluorine reacts vigorously with sodium and potassium hydroxides, but that the solid becomes coated with a layer of fluoride which decreases considerably the velocity of the process. It also appears that many oxides are not attacked at ordinary temperatures, and a difference between the behavior of oxides and hydroxides has been clearly demonstrated by Rengade,[2] who has found that sodium and potassium oxides are unreactive.

Experimental

A magnetically operated pump was used to circulate fluorine in a closed system consisting of a reservoir of capacity about twelve liters, a mercury manometer and a reaction chamber which contained a pulverized oxide or hydroxide. The chamber was immersed in a bath, at the desired temperature. The manometer permitted one to follow the reaction, and the apparatus in direct contact with the gas was entirely of metal, for the most part either nickel or Monel metal. After all, or nearly all, of the fluorine had been used up, a condition which could be recognized by the fact that the pressure remained constant at about half of its initial value, a sample of the gaseous reaction product was condensed and was analyzed by a fractional distillation method similar to that described by Podbielniak.[3] The different gases were collected and measured in separate flasks and, when sufficiently abundant, were later identified. Oxygen and oxygen fluoride were easily recognized by the vapor pressures, the vapor densities, the color of the liquids, the odor and the ability to react with a solution of potassium iodide.

Each distillation revealed a small amount of material which existed as a white solid at the temperature of liquid air, was less volatile than oxygen fluoride, but evaporated at low temperatures. The variable vapor densities, ranging between 60 and 98, which were obtained, as well as the fact that no sharp melting point was observed, indicated that a mixture had been encountered. The amount was never large enough to permit the separation and identification of the compounds by the methods readily available.

It is not necessary to conclude that this mixture was produced by the reaction with the oxide or hydroxide. The substances may have re-

---

[1] Moissan, "Le Fluor," Paris, 1900, p. 228.

[2] Rengade, *Compt. rend.*, **144**, 753 (1907).

[3] Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931).