drogen decreases, since the "solubility" of small bubbles is greater than that of larger ones. The electrolyte immediately surrounding the growing bubble is, therefore, less concentrated than at points on the surface of the electrode removed from the bubble. These differences of concentration produce short-circuited concentration cells, the operation of which results in the formation of hydrogen ion from dissolved molecular hydrogen at points where the latter is more concentrated, and the reverse reaction at the bubble or in the adjacent electrolyte.

4. Summary.

The increase of hydrogen overvoltage with diminished pressure is shown to follow, in a nearly quantitative manner, from the theory advanced by MacInnes and Adler.

A study has been made of the effect of change of gaseous pressure on several chemical processes involving the evolution of hydrogen. The changes in rates of reaction and in reaction efficiencies were found in each case to be in the directions which follow from the change of hydrogen overvoltage with pressure, *i. e.*, a decrease of gaseous pressure produces (*a*) a decrease of the rate of solution of metals in electrolytes, (*b*) an increase in the efficiency of reductions by metals, and (*c*) an increased efficiency of metal deposition.

The theory explaining the fluctuation of overvoltage accompanying the evolution of a single bubble from a platinum electrode is more fully discussed.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE EFFECT OF PRESSURE, AND OF DISSOLVED AIR AND WATER ON THE MELTING POINT OF BENZENE.

BY THEODORE W. RICHARDS, EMMETT K. CARVER AND WALTER C. SCHUMB.

Received October 16, 1919.

The need of a large number of accurately determined fixed points for standardizing thermometers is too well understood to need comment. The transition temperatures of the hydrated salts seem to be the points best suited for this purpose, although the freezing points of pure liquids are also convenient. To give a useful fixed point the liquid adopted must not only be one that may be easily and surely purified, but it must also have a high latent heat of fusion. This last is important for two reasons: because such a substance sooner compensates for loss of heat through the walls of the container or gain from stirring, and because the effect of impurities on the freezing point is inversely proportional to the latent heat of fusion.

Although benzene is less satisfactory in these respects than water, nevertheless it is by no means to be rejected as a means of fixing a thermometric point.

With this in mind, one of us, with the assistance of J. W. Shipley,[1] recently determined with care the freezing points of two carefully prepared samples of pure benzene (from coal tar and from benzoic acid) and found the same very constant point for each, namely, 5.483° ± 0.002°. The measurements were made in the Beckmann apparatus with carefully calibrated thermometers.

The point thus determined is evidently of sufficient constancy to serve the purpose in mind; nevertheless it is not, of course, the true triple point of benzene. The determination was made under atmospheric pressure; moreover, as J. Meyer[2] has rightly pointed out, the liquid contained dissolved air. For the object sought, these circumstances make no difference, if only the pressure and saturation of dissolved air are constant. The essential feature is convenient and exact reproducibility of the point. Meyer's objection that the concentration of the dissolved air varies is (as will be shown) not well taken, since during the production of the amount of solid required for a satisfactory observation, enough air is displaced from the crystals to saturate fully the remaining liquid. Hydrogen from the decomposition of water by the sodium used in drying could not have been present, since it must have escaped during the distillation.

In order to place the matter in a more satisfactory situation, the effect of the dissolved air has been studied, as herewith detailed. The procedure adopted was first to determine the freezing point of benzene under its own vapor pressure, and then, to admit dry air at atmospheric pressure and take the temperature when the benzene became saturated.

To protect the thermometer from the change in pressure when air was admitted, it was immersed in mercury in the inner open tube of a double-walled test-tube, whereas the benzene was placed in the outer compartment, between the walls. Just above the mercury in the inner tube was a layer of carbon tetrachloride which served to protect the mercury from loss of heat, and the whole apparatus was protected from too rapid heat-exchange by means of an air jacket. An iron stirrer plated with silver, in the benzene, was lifted and dropped by means of an electromagnet operated by a metronome and relay. The whole was placed in a thermostat at about 5.3° to 5.6°.

The apparatus was filled through a ground joint, which was then closed and sealed with mercury. A trap caught any benzene which had distilled into contact with the stopcock leading to the pump. At first a

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[1] T. W. Richards and J. W. Shipley, This Journal, **36**, 1825 (1914).

[2] J. Meyer, *Z. physik. Chem.*, **90**, 721 (1915). See also Garelli and Falcioli, *Atti accad. Lincei*, [1] **13**, 110 (1904); also Prytz and Holst, *Wied. Ann.*, **54**, 130 (1895).

Beckmann thermometer was used, but was found unsatisfactory owing to the uncertainty of the stem correction. In later determinations an old, very accurate and sensitive Baudin thermometer with a large bulb was used. Finally the point on the international scale was determined by standard Baudin thermometers Nos. 15200 and 15276.

Determinations were made as follows: The apparatus was filled about half full of benzene, which was frozen solid. The disengaged air was pumped off (the evacuation being continued to minimum pressure), and the benzene was melted and frozen again. After a second evacuation very little, if any, air remained. Finely divided crystals, highly satisfactory for the purpose, were produced by supercooling the liquid benzene several degrees and stirring. The automatic stirring was continued, and the solid phase augmented; but until there was so much solid benzene that the motion of the stirrer was prevented, the temperature remained unchanged. This proved that no air remained, since otherwise the temperature would have fallen slowly as the liquid diminished. By varying the rate of stirring over a wide range it was shown that the heat of stirring had no appreciable effect on the apparent melting point.

When the triple point had thus been fixed, and the quantity of crystals best suited to give a constant point had developed, air dried over sulfuric acid was admitted. The freezing point immediately rose about 0.028°, since benzene freezes at a higher temperature under high pressure than under low pressure. As the stirring continued, the temperature fell because of the air dissolved, at first rapidly, and then more slowly, in a well-defined curve, of which a typical graph follows.

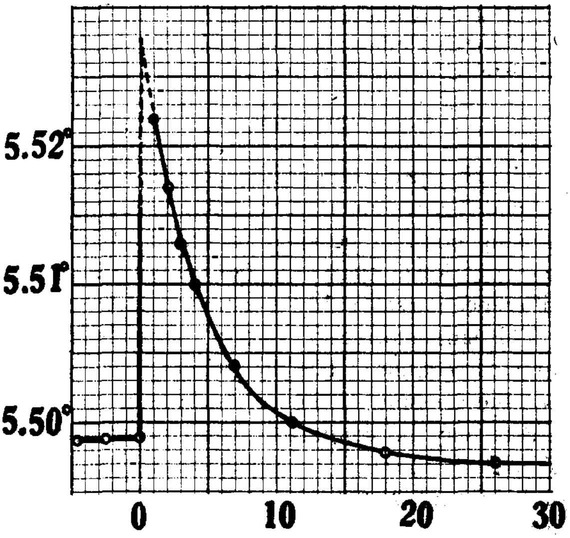

Fig. 1.—Typical diagram showing fall of temperature caused by solution of air in pure benzene.

Ordinates represent temperatures; abscissas represent time in minutes. The initial maximum temperature is attained only with complete absence of stirring, and then only for a brief time. During the trial indicated the stirring was continuous and equable.

In this manner, after a few preliminary trials, the following 5 successive determinations were made. The 3 samples of benzene referred to in the table were prepared as follows: For

Expts. 1 and 2 the benzene was shaken with 5 successive portions of conc. sulfuric acid. Then followed several washings with a solution of sodium hydroxide and several successive portions of water. It was subsequently dried over calcium chloride and sodium, distilled, recrystallized 5 times, and kept over sodium. Successive portions of this metal were needed to eliminate all the water. The material used for Expts. 3 and 4 was identical with Shipley's Sample C, and that used in the fifth determination was identical with Shipley's Sample B. The former had been crystallized 4 times and the latter 6.[1] Both had been kept 3 years over sodium, and all were distilled directly into the freezing-point apparatus. Below are recorded the results, corrected to the hydrogen standard of temperature as given by the mean of the readings of thermometers Baudin 15200 and 15276, making due correction for the effect of changing atmospheric pressure on the thermometer bulb and all other known causes of error.

TABLE I.—DIFFERENCE BETWEEN FREEZING POINT IN VACUUM AND IN AIR.

	Degrees centigrade.		Difference.
	In vacuum.	In air.	Vac.—Air.
(1) Benzene as described above	5.504	5.502	0.002
(2) Benzene as described above	5.502	5.498	0.004
(3) Shipley's synthetic benzene (4th)	5.498	5.496	0.002
(4) Shipley's synthetic benzene (4th)	5.500	5.496	0.004
(5) Shipley's coal-tar benzene (6th)	5.499	5.497	0.002
Average	5.5006	5.4974	0.003

The absolute value will be considered in detail later. The important outcome of figures given in the table is the fairly consistent evidence that the melting point of benzene saturated with air under atmospheric pressure is 0.003° lower than the true triple point of pure benzene, and that the difference is reasonably constant, and trustworthy.

This small correction (0.003°) is made up of two almost equal opposing large corrections. The presence of dissolved air lowers the freezing point, but the pressure of the atmosphere increases it. The latter of these two effects may be computed from the well known equation of Clapeyron: $dT/dP = T\Delta v/L$. According to the carefully executed determinations of J. Meyer, one g. of benzene on melting takes in 30.48 average calories, and increases its volume by 0.1333 cm.[2] This gives $dT/dp = 0.0295$ degree per atmosphere. Tammann's direct measurement[3] between 0 and 500 atmospheres gives $dT/dp = 0.028$ degree per atmosphere, but

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[1] THIS JOURNAL, **36**, 1830 (1914).

[2] J. Meyer, *Z. physik. Chem.*, **72**, 246 (1910).

[3] Tammann, *Krystallisieren und Schmelzen*, Leipzig, 1903, p. 197; see also *Wied. Ann.*, **66**, 486 (1898).

on making due allowance for curvature of the line depicting the change with pressure, it would appear that his result at atmospheric pressures must almost exactly agree with that computed above. The average change of pressure in the 5 experiments was from 35.4 mm. (the pressure of benzene vapor at its triple point) to 762.4 mm. (the average barometer) or 727 mm. This change should then alter the freezing point by $(727/760)0.0295^\circ = 0.0282^\circ$.

Taking 0.028° as the pressure effect, 0.031° is computed (by the addition of 0.003°) as the depression of the freezing point due to air dissolved in benzene under atmospheric pressure. The weight of air dissolved in the benzene may be estimated from this result by the familiar equation, $w = MW\Delta t/k$, which gives 0.017 g. or 13 cc. of air dissolved in 100 cc. of benzene. It was found by Just[1] that 11 cc. of nitrogen at 760 mm. pressure dissolved in 100 cc. of benzene at 20°, but he made no trial with oxygen. Probably oxygen is somewhat more soluble than nitrogen, hence Just's result is of the same order as ours. The estimate of 63.5 cc. of air per 100 g. of benzene (corresponding to a depression of 0.14° in the freezing point) made by Meyer,[2] is evidently excessive. Meyer's conclusion rested on only a single experiment, made as a side issue in a research having another object, and no evidence is afforded that water was excluded from the benzene in this experiment, an especially insidious source of error in cases like this, as will be shown.

Evidently the melting point of benzene saturated with dry air, under atmospheric pressure, should be an unusually constant point, being much less affected than most freezing points through change of pressure. A rise in the barometer, for example, produces a rise in freezing point through increase of pressure but is accompanied by a proportional increase of dissolved air; each of the opposing almost equal corrections is augmented to almost the same extent. A change of $^1/_4$ of an atmosphere would be needed to change the freezing point of the air-saturated liquid by as much as 0.001°.

As already stated, the graph above indicates that saturation with air is attained rather quickly by freezing benzene agitated by a splashing stirrer. But, on the other hand, is there danger of supersaturation? Liquids are well known to become easily supersaturated with gases, and it is not impossible that benzene saturated with air might become supersaturated as it becomes partly solidified. The ultimate constancy of the freezing point of benzene saturated with air as found both in the earlier research and in the present one shows, however, that the supersaturation is adequately relieved by suitable stirring.

As already stated, another possible source of error or uncertainty in

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[1] Just, *Z. physik. Chem.*, **37**, 361 (1901).

[2] J. Meyer, *Ibid.*, **72**, 238 (1910).

the freezing point of benzene is the presence of water. This is a danger to be especially feared in taking the freezing point of any non-aqueous liquid below the dew point of the air of the laboratory, since water then readily condenses and dissolves in the other liquid. Hence, experiments were instituted in order to determine the effect on the freezing point of benzene of saturation with water, as well as to estimate cryometrically the extent of its maximum solubility at the freezing point.

The literature on the subject is widely divergent in its verdict. One of the early papers, by Herz,[1] states that 0.211 volume of water are taken up at 22° per 100 volumes of benzene (about 87.6 g.). This would correspond to a depression of nearly 0.7° in the freezing point. From our own results, as will be seen, it must be clear that this result is far too large. One cannot help thinking that according to his method of experimentation (which consisted in dropping water into benzene until an excess appeared) an unnoticed film of water must have clung to the glass of the vessel containing the benzene. Considerably better, but still possibly somewhat subject to the same cause of error, were the results of Groschuff.[2] He found that 100 g. of benzene dissolves 0.03 g. of water at 3°, and 0.061 g. at 23°; from which we may conclude that at 5.5° about 0.04 g. of water is taken up, corresponding to a depression of about 0.13°.

A safer method seems to be the determination of the effect of water in excess on the freezing point of benzene. According to a recent statement by Wm. J. Jones,[3] Dr. N. V. Sidgwick states that the freezing point of water-saturated benzene is about 0.1° below that of pure benzene. Our own experiments verify this statement, as is seen by the following figures for two separate trials.

	Arbitrary. Beckmann.	Standard Baudin. No. 15,276.
Temperature of freezing before addition of water, degrees	4.403	5.485 (cor'd)
Temperature of freezing when saturated with water, degrees	4.310	5.389
Difference, degrees	0.093	0.096
		Mean 0.095

If the cryoscopic constant for benzene is taken as 5000, this would correspond to a solubility of 0.034 g. of water per 100 g. of benzene at 5.5°, not far from Groschuff's value.

Evidently an amount of water corresponding to only 1% of the amount in the saturated solution is enough to produce an effect on the freezing point of 0.001°, therefore, great care must be taken to exclude water. Sodium added to benzene containing a trace of water of course evolves

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[1] Herz, *Ber.*, **31**, 2669 (1898).

[2] Groschuff, *Z. Elektrochem.*, **17**, 348 (1911).

[3] W. J. Jones, *J. Soc. Dyers and Colourists*, **35**, 46 (1919).

hydrogen, and soon becomes coated with sodium hydroxide, when it is less efficient. Accordingly, freshly prepared sodium must be added in successive portions in order to obtain complete dryness in any reasonable time. We found that if perhaps 2 g. of sodium wire is added to 50 cc. of benzene on each of 2 successive days, the liquid is sufficiently dry so that a third portion of added sodium allowed to stand for 2 days more, produces no observable effect upon the freezing point. The fear that sodium thus added in the presence of traces of water might produce a trace of a hydrobenzol does not seem to be substantiated by our experience.

Benzene thus dried must be scrupulously protected from contact with moist air, and all the apparatus which it touches must have been previously heated in a current of dry air in order to exclude traces of water. All these precautions were observed in the work upon the exact freezing point of benzene which follows. No correction was made for the possible solution of carbon dioxide in benzene. The solubility of this gas in the liquid under atmospheric pressure is hardly great enough to make the amount dissolved under its usual partial pressure of 0.0003 atm. appreciable.[1]

The freezing point of benzene as newly found is distinctly higher than those observed by one of us in collaboration with Barry, Davis, and Shipley. Although the object of the present experiments had not at first been to determine the precise value, but only the effect of air, nevertheless the difference obviously suggested further research. Accordingly very careful new absolute determinations of the freezing point of benzene were made, taking account of all the precautions suggested in the foregoing pages.

In repeating the work on the true freezing point of dry benzene saturated with air, a Beckmann freezing-point apparatus was used. The standard Baudin thermometers dipped directly into the mixture of solid and liquid benzene, which was stirred by hand with a platinum-glass stirrer. Air (thoroughly dried by conc. sulfuric acid) was passed continuously through the upper part of the test-tube. The outer bath was kept between 5.0° and 5.5°, approaching the latter point in the final determinations. The distillation of the purified benzene was carried out by electric heating in a glass-stoppered double-necked distilling flask[2] and the distillate could be collected in either one of two receiving test-tubes, at the end of a Y-branched condenser tube, by the expedient of tilting the flask from side to side The test-tube containing the second fraction of the distillate, of which the

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[1] It was found by Just that benzene dissolves about 2.5 times its volume of carbon dioxide (a result which some results of ours seem to show to be excessive) but even if the gas is as soluble as this, the liquid should take out of ordinary air only about a millionth part of its weight of gas.

[2] T. W. Richards and F. Barry, THIS JOURNAL, 36, 1787 (1919).

freezing point was to be determined, was supplied with a cork stopper fitted with the stirrer and standard thermometer all in place, and could be detached from the condenser tube at a ground joint, immediately afterwards being connected to a supply of dry air.

Pure coal-tar benzene had been prepared as usual and was further recrystallized 3 times and dried over successive portions of sodium for 2 days at a time. Synthetic benzene had been prepared from benzoate[1] and had been further purified by Dr. Shipley; it was yet further recrystallized 3 times and dried over sodium as in the case of the coal-tar product. For the determination of the ice-point, natural fresh-water ice of good quality was chopped into small lumps, allowed to stand in a beaker until a part of it had melted, then drained and the interstices filled with pure, chilled water before the final reading.

After the purified benzene had stood, as described, over sodium in the distilling flask for several days, it was carefully distilled directly into the test-tube, the first third being collected separately. The benzene all distilled within 0.05°. The test-tube having been disconnected from the condenser at the ground joint and connected to the dry air current, the tube was allowed to cool in an ice bath. By sufficiently supercooling (to about +1°) about a third of the liquid could be instantly frozen in the form of small, flaky crystals; and by further alternately cooling and briefly warming the tube, the quantity of solid could be increased until the whole tube was filled with a thin paste of crystals. The intermittent warming was necessary to cause the solid cakes on the walls of the tube to become disengaged and permit movement of the stirrer. When a paste of the desired consistency had been obtained, the outside of the test-tube was wiped dry and the latter placed in the air-jacket, which was suspended in the cooling bath. Pieces of absorbent cotton were placed about the neck of the test-tube to keep it in place and prevent air currents within the air-jacket. The bottom of the test-tube rested likewise on a pad of cotton. The mixture of solid and liquid benzene was frequently stirred, and the temperature of the thermometer read by means of a cathetometer, which was carefully adjusted. The thermometer was always maintained in a vertical position as tested by a plumb-line, and at a definite distance from the cathetometer objective. In some experiments with Baudin No. 15276 the top of the mercury thread was allowed to just emerge above the top of the cork stopper in the mouth of the test-tube; in one trial (No. 15200 being used) the meniscus was read through the glass of the test-tube, just below the bottom of the stopper; in this case the stem correction was wholly negligible. In all cases the proper stem corrections were calculated, knowing the length and mean temperature of the several portions of projecting thread, both within and above the cork stopper.

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[1] Under the kindly undertaken direction of Professor E. P. Kohler.

The freezing point was constant over at least an hour's time in each case, and did not alter appreciably from the initial readings: since the amount of solid had increased in every case by about 25–30%, this constancy is indicative of the purity of the substance.

After a determination had been completed, the benzene was allowed to melt in a current of dry air, and replaced in a bottle over sodium.

The two standard Baudin thermometers used in making the final measurements differed somewhat in their readings when all appropriate corrections had been applied. When a graph of the calibration corrections was made for each thermometer, it was found that unfortunately, from the nature of the curves, just at 5.5° the uncertainty of each was greatest, and in either or both a possible error of 0.003° or more might exist. Therefore the two thermometers were carefully compared with one another, by simultaneously immersing them in a mixture of solid and liquid benzene, and subsequently in a bath of cracked ice and pure water. In this way it was found that No. 15200 reads 0.014° higher than No. 15276 at 5.5°. The mean value was taken as the best available. This mean is obviously subject to an uncertainty of at least ±0.007 due to the calibration of the thermometers alone, apart from any further uncertainty due to the quality of the benzene.

FREEZING POINT OF DRY BENZENE (SATURATED WITH AIR).
Degrees Centigrade.

Number of thermometer.	No. 15,276.	No. 15,200.
(1) Coal-tar benzene (Carver's)	5.487	...
(2) Coal-tar benzene dried 2 days longer	5.487	...
(3) Same as (2)	5.488	5.499
(4)		
(5) Coal-tar benzene	5.487	5.501
(6)		
(7) Same as preceding	5.488	5.501
(8)		
(9) Same, one thermometer only used	...	5.499
(10) Same, one thermometer only used	5.485	...
Averages	5.487	5.500

Total average of both thermometers 5.493.

The outcome shows that the most probable freezing point of benzene saturated with air is 5.493°, therefore, the true triple point is 5.496°. We are inclined to think that these values (about 0.01° higher than those based on the earlier determination) are the more accurate, since they represent the averages of the readings on two standard thermometers (instead of only one), and since most of the probable errors tend to lower rather than to raise the melting point. Nevertheless as already stated neither of the new values can be considered as certain within a much narrower limit than 0.01°, because of the unfortunate irregularity of the two standard thermometers in this neighborhood. Moreover in spite of the use of many different specimens of benzene, the doubt must always remain as to whether the samples employed were perfectly pure. That our material was purer than the specimen employed by J. Meyer is shown by the fact that our melting point is over 0.05° higher than his (5.44°). The preparation of any organic substance in a state of great purity is difficult, although benzene is more promising in this respect than the great majority, because of its convenient crystallization, its easy preparation, and its considerable stability. For a closer evaluation of the melting point of benzene, a prolonged and laborious investigation would be needful, for which we have not time at present. In the meantime it is safe to say that either the triple point, or the freezing point when saturated with air, is easily attained and very constant.

We are glad to express our obligation to the Carnegie Institution of Washington for pecuniary support in this research.

Summary.

1. Benzene saturated with air under atmospheric pressure melts 0.003° below the true triple point.
2. Benzene thus saturated has its freezing point but little altered by change of pressure.
3. Evidence of an important degree of supersaturation does not appear.
4. The effect of pressure in the absence of dissolved air is shown to alter the freezing point 0.029° per atmosphere.
5. Saturation with water lowers the freezing point of benzene 0.095°.
6. The true freezing point of benzene saturated with air is probably not far from 5.493°, and the true triple point not far from 5.496°.

CAMBRIDGE, MASS.

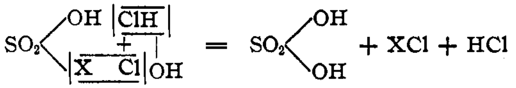
[CONTRIBUTION FROM THE UNIVERSITY COLLEGE OF SCIENCE OF CALCUTTA.]

HALOGENATION. XIX. THE REPLACEMENT OF SULFONIC GROUPS BY CHLORINE AND THE PREPARATION OF ORGANIC CHLORO-DERIVATIVES.

BY RASIK LAL DATTA AND HARAPARBUTTY KUMAR MITTER.

Received April 14, 1919.

It has been found that when a current of chlorine gas is introduced into an aqueous solution of sulfonic acid, the sulfonic group is detached with the simultaneous production of the corresponding chloro-derivative. The reaction that takes place may be represented as follows:



$$\mathrm{SO_2}\left\langle\begin{array}{ll}\mathrm{OH} & \boxed{\mathrm{ClH}} \\ & \;\;+ \\ \boxed{\mathrm{X\quad Cl}} & \mathrm{OH}\end{array}\right. = \mathrm{SO_2}\left\langle\begin{array}{l}\mathrm{OH} \\ \\ \mathrm{OH}\end{array}\right. + \mathrm{XCl} + \mathrm{HCl}$$

where X represents the organic radical to which the sulfonic group is attached.