shows that it is then necessary to assume that the colored form of the indicator is produced in appreciable quantity only when the second hydrogen of the indicator acid has been replaced by the base.

4. Neutral salts are shown to have a great effect on the fraction of the indicator transformed (as determined by its color) and correspondingly on its ionization constant; thus the value of the constant is doubled by increasing the salt concentration from 0.03 to 0.40 normal. The change of the constant K_I (regarding the indicator as a monobasic acid) with the total salt concentration C_S can be expressed by the equation $K_I = 0.77 \times 10^{-10}[1 + 2.8(C_S\gamma)^{0.5}]$, in analogy with the expression for the deviations shown by strong electrolytes.

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A SUMMARY OF THE SPECIFIC HEATS OF GASES.

BY GILBERT N. LEWIS AND MERLE RANDALL.

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In free energy calculations over a wide range of temperature, the specific heats play a very important role. Most of the important chemical equilibria which have been studied at high temperatures involve gaseous substances. It is therefore necessary to consider with care what values are to be attributed to the specific heats of those common gases which enter into many important chemical reactions. Professor Haber[1] has given an admirable treatment of this whole subject, but since the publication of his book several important experimental investigations in this field have appeared. It is therefore desirable to review the whole subject of gaseous specific heats, and to select for further reference formulas which will represent the most probable values of the specific heats of the more important gases over a considerable range of temperature.

The methods which have been employed in determining the specific heats of gases may be divided into three groups: The first comprises what we may call the direct methods in which a hot gas is led directly into a calorimeter. The second includes a number of methods such as the one used in the celebrated experiments of Kundt and Warburg, the method of Clément and Desormes, and the method of Lummer and Pringsheim. This group of methods we will call the adiabatic, since they all involve the change of pressure, volume and temperature when a gas is compressed or expanded adiabatically. The calculation of the specific heat by any of these adiabatic methods requires the assumption of the complete validity of the gas law.

[1] "Thermodynamics of Technical Gas Reactions." English Translation by Lamb; Longmans, Green & Co., 1908.

The third group comprises what may be called the explosion methods, developed by Bunsen, Mallard and Le Chatelier, Berthelot and Vieille, and Langen. In all these methods an explosive mixture of gases is ignited and the maximum pressure thus developed is ascertained. By adding to the explosive gases other inert gases, their specific heats may be determined over a wide range of temperatures. These methods suffer, however, the disadvantage that they do not permit the study of a single gas, but always of a gaseous mixture. For a full discussion of these various methods and the experimental difficulties to which they are subject, and also for a bibliography of the earlier work on the specific heats of gases, we may refer to the treatise of Haber, which we have already mentioned.

Monatomic Gases.

We shall find it convenient to classify the various gases according to the number of atoms in their molecules.

The prediction of the heat capacity of the monatomic gases was one of the most striking achievements of the kinetic theory. According to this theory the heat capacity at constant pressure of a mol of any monatomic gas should be independent of the temperature and equal to five calories per degree.[1] This prediction was verified in the case of mercury vapor by the classical experiments of Kundt and Warburg. Argon and helium were shown by their discoverers[2] to have a molal heat of about 5, and were therefore regarded as monatomic. The experiments on argon were repeated by Niemeyer,[3] who obtained identical values for the molal heat capacity, at 0°, 13° and 100°, namely, 4.99. Behn and Geiger[4] reinvestigated helium for which they obtained the molal heat, 5.1. All of these investigators made use of adiabatic methods, but their results are corroborated by the recent work of Pier,[5] who investigated argon by an explosion method over the range from 0° to 2350° and obtained for the average molal heat the value 4.96.[6]

On the basis of these experiments we will adopt for the molal heat at constant pressure of all monatomic gases at all temperatures, the round value, $C_p = 5.0$.

Diatomic Gases.

Nitrogen.—The specific heat of this gas has been more studied than any other. The most recent experiments are those of Holborn and Austin[7]

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[1] More accurately, 4.97 cal.

[2] Rayleigh and Ramsay, *Proc. Roy. Soc.*, **57**, 265 (1895); Ramsay, *Ibid.*, **58**, 81 (1895).

[3] Niemeyer, Diss. Halle, 1902.

[4] Behn and Geiger, *Ber. physik. Ges.*, **5**, 657 (1907).

[5] Pier, *Z. Elektrochem.*, **15**, 536 (1909).

[6] Landolt and Börnstein give also a value 4.92 obtained by Dittenberger (Diss. Halle, 1897).

[7] Holborn and Austin, *Abh. Physik. Tech. Reichsanstalt.*, **4**, 131 (1905).

up to 800°, those of Holborn and Henning[1] up to 1600° and those of Pier[2] to 2300°. All show the specific heat of nitrogen to be a linear function of the temperature, but the values of Pier agree with those of Holborn only in the neighborhood of 1800° At lower temperatures the values obtained by Holborn and his collaborators are lower than those of any other observers. They find at the centigrade zero,[3] $C_p = 6.58$. Pier's equation gives 6.89. There is almost no doubt that the value of Holborn is too low, Regnault obtained the value 6.72 and Masson by an adiabatic method 6.86. We will take the mean of all these values, namely, $C_p = 6.76$. Combining this value with the one obtained by Pier and by Holborn and Henning at 2000°, we obtain the formula $C_p = 6.49 + 0.0010T$. We shall find in the case of other diatomic gases as in this case that the molal heat at the absolute zero does not differ from the value 6.50 except by amounts which are well within the limit of experimental error. We shall therefore, for the sake of convenience in calculation, adopt the practise of Le Chatelier, and of Nernst, and take this value as the molal heat at the absolute zero of all the diatomic gases. We may therefore modify the above equation by this negligible amount and write

$$C_p = 6.50 + 0.0010T.$$

Oxygen.—The various determinations of the specific heat of oxygen may be satisfactorily expressed by the same equation as for nitrogen.

$$C_p = 6.50 + 0.0010T$$

This gives at centigrade zero the value 6.77. Regnault found 6 85, Pier 6.89 and the mean of several adiabatic determinations is 6.89.[4] At 2000° our equation gives 8.77 while Pier obtained 8.70. The higher values obtained by Holborn and Austin between 0° and 800° need not be considered as they were determined indirectly from measurements on mixtures of oxygen and nitrogen, and are not consistent among themselves.

Hydrogen.—For this gas we will adopt the formula

$$C_p = 6.50 + 0.0009T.$$

This gives at 0° C. the value 6.75. Regnault's value is 6.76, that of Wiedemann 6.87, while Pier's equation gives 6.69. The adiabatic method in this case gives altogether too high a result, 7.05, due perhaps

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[1] Holborn and Henning, *Ann. Physik.*, [4] 18, 739 (1907); [4] 23, 809 (1907).

[2] Pier, *Z. Elektrochem.*, 15, 536 (1909).

[3] Both Holborn and Pier expressed all their results in terms of mean specific heats and centigrade temperatures. Before comparing their results we have in every case transformed their equations into others involving true specific heats and absolute temperatures.

[4] The agreement of these values at 0° C. among themselves and the agreement between Pier's results at high temperatures and those of Le Chatelier and of Langen indicate that a somewhat more exact equation than the one we have employed would be obtained by taking the molal heat at absolute zero higher than 6.5 or by introducing in the formula a term involving T^2.

to the high thermal conductivity of hydrogen. Our equation gives a 2000° C. the value 8.55 whereas Pier's gives 8.50.

Carbon Monoxide, Nitric Oxide.—These gases have not been investigated over any large temperature range. The existing data are in satisfactory agreement with the equation obtained for nitrogen, namely,

$$C_p = 6.50 + 0.0010T.$$

Hydrogen Chloride, Bromide, Iodide—In these cases also, although the few existing data are far from concordant with one another, the most probable values seem to agree with the nitrogen formula,[1]

$$C_p = 6.50 + 0.0010T.$$

Chlorine, Bromine, Iodine—The existing data concerning the halogens are far from adequate but suffice nevertheless to show that the molal heats of these three gases are considerably higher than those of the other diatomic gases which we have discussed. There is little evidence that these molal heats approach the same value at the absolute zero as the others, nevertheless the existing data do not disprove this assumption, and we shall therefore in this case also take 6.5 as the molal heat at the absolute zero. Regnault found the average molal heat of chlorine between 20° and 200° to be 8.6 and of bromine between 83° and 228°, 8.9. Assuming that the molal heats vary linearly with the temperature, approaching 6.5 at the absolute zero, we find at 0° C. for chlorine, $C_p = 8.1$, for bromine, $C_p = 8.0$. Martini[2] at 0° C. found 7.9 for chlorine by an adiabatic method, by a similar method Strecker[3] investigated the three halogens between room temperature and 375°. If we should place complete reliance upon his results we should be forced to conclude, contrary to our assumption, that the specific heats of the halogens are nearly independent of the temperature, but his individual values differ so widely from one another, especially at the higher temperatures, that we cannot give great weight to his conclusions. The averages of all of Strecker's measurements[4] reduced according to our assumption to 0° are 7.5 for chlorine, 8.1 for bromine, and 7.2 for iodine A later adiabatic determination of the specific heat of iodine by Stevens[5] gives 7.5 when reduced to 0° C. Pier[6] has determined the specific heat of chlorine by his explosion method. The method however was not then developed in its final form and there is considerable doubt as to whether much weight can be given to these

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[1] Additional evidence that the molal heat of hydrogen chloride is the same as that of other permanent diatomic gases is furnished by the experiments of Pier, *Z. physik. Chem.*, **66**, 759 (1909).

[2] Martini, *Phil. Mag.*, [5] **39**, 142 (1895).

[3] *Ann. Physik.*, [3] **13**, 20 (1881).

[4] Strecker also cites a few measurements of the specific heat of chlorine made by Kundt which agree substantially with his own.

[5] Stevens, *Ann. Physik.*, [4] **7**, 285 (1902).

[6] Pier, *Z. physik. Chem.*, **62**, 385 (1908).

results, which, like those of Strecker, indicate a small temperature coefficient. We shall adopt for these three gases the expression

$$C_p = 6.5 + 0.004T.$$

It is not unlikely that later experiments will show either that our value of 6.5 at the absolute zero is low or more probably that the molal heat of these gases can only be adequately expressed by a quadratic formula which will make the temperature coefficient diminish with increasing temperature.

Triatomic Gases.

Water.—The earlier values of the specific heat of water vapor differed widely, and we may base our discussion of this case chiefly upon the recent experiments of Holborn and Henning[1] and of Pier.[2] We have plotted the values obtained by these observers, and after fully considering the experimental methods, and allowing for a slight dissociation of water at the higher temperatures (which was not entirely excluded in Pier's experiments), we have chosen the following formula for the molal heat of water vapor between 0° and 2000°:[3]

$$C_p = 8.81 - 0.0019T + 0.00000222T^2$$

The extreme deviation of this formula from those of Holborn and Henning and of Pier is 4.5%, but throughout almost the entire range the differences do not exceed 2.7%. Our curve shows a minimum at about 150°, and in fact Thiesen[4] from measurements on the velocity of sound in water vapor concluded that the specific heat reached a minimum in the neighborhood of 80°. Holborn and Henning's equation gives a minimum at a somewhat higher temperature, while Pier's shows no minimum at all.

Hydrogen Sulfide.—With a gas so imperfect as hydrogen sulfide, little reliance can be placed upon adiabatic determinations of the specific heat. In as far as they go, these values seem to corroborate the only direct measurement, that of Regnault, who found 8.3 for the molal heat of hydrogen sulfide at 110°. This is precisely the value given by our formula for water vapor. For this reason and because of the chemical resemblance between water and hydrogen sulfide, we will assume, until further experimental evidence is available, that the molal heat of hydrogen sulfide follows the same formula as that of water, namely,

$$C_p = 8.81 - 0.0019T + 0.00000222T^2.$$

Carbon Dioxide.—In this case also we may rely chiefly upon the measurements of Holborn and Austin, Holborn and Henning, and those of Pier.

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[1] Holborn and Henning, *loc. cit.*

[2] Pier, *Z. Elektrochem.*, **15**, 536 (1909); **16**, 897 (1910).

[3] Since these calculations were made, Bjerrum (*Z. physik. Chem.*, **79**, 513, 537 (1912)) has published investigations on the specific heat of water vapor and carbon dioxide, but carried on at temperatures higher than we are here considering.

[4] Thiesen, *Ann. Physik*, [4], **9**, 88 (1902).

Pier's calculations were not altogether independent as he made use of the equation given by Holborn. Pier considers however that his measurements corroborate those of Holborn at the lower temperatures and furnish material from which the specific heats at the very highest temperatures may be estimated. We have plotted the data of Holborn together with the equation given by Pier and as in the case of water vapor we have determined what quadratic formula[1] best represents the molal heat of carbon dioxide between 0° and 2000°. The formula chosen[2] is

$$C_p = 7.0 + 0.0071T - 0.00000186T^2.$$

Between 0° and 1200° the maximum deviation of this formula from those of Pier and Holborn is hardly more than 1%. At 2000° the value obtained from Pier's equation is 2% higher than ours. That obtained from Holborn's is 9% lower. The value given by our formula at 0° is 8 8, which is somewhat higher than any of the older values, that of Regnault was 8.3, that of Wiedemann 8.6, and numerous adiabatic determinations average about 8.5.

Sulfur Dioxide.—The work of Fürstenau[3] seemed to indicate a close resemblance between the molal heats of sulfur dioxide and carbon dioxide. This has been demonstrated by Pier who could find no difference between the behavior of carbon dioxide and of sulfur dioxide over a wide range of temperature. We shall therefore use for the latter the same equation as for the former, namely,

$$C_p = 7.0 + 0.0071T - 0.00000186T^2.$$

Polyatomic Gases.

Ammonia.—Regnault found for the molal heat of this gas the value 8.8 at 120°. Wiedemann obtained the values 8.88 at 61° and 9.14 at 114°. Numerous adiabatic determinations have been made which in the average agree with these direct determinations. Thus Wüllner at 0° and 100° found respectively 8.55 and 9.07. Recently the molal heat of ammonia has been determined at 466° and 480° by Nernst,[4] who found 10.4 and 11.2, respectively In the same paper he cites measurements at 20° made by Keutel and by Voller, who found the value 8.63. All of these measurements, within the limits of experimental error, fall on a straight line given by the formula

$$C_p = 7.5 + 0.0042T.$$

Other Gases.—We have given formulas for the molal heat of all important gases for which we have measurements that are at all reliable. In the

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[1] The equations given by Pier both for carbon dioxide and for water vapor contain terms in T^3.

[2] Since this formula was chosen we have found recent measurements by Swan (*Proc. Roy. Soc.*, (*A*) **82**, 147 (1910)) at 20° and 100° which agree with our formula within 2% and 1%, respectively.

[3] Fürstenau, *Ber. physik. Ges.*, **6**, 968 (1908); **7**, 137 (1909).

[4] Nernst, *Z. Elektrochem.*, 16, 96 (1910).

course of our later calculations it will be necessary to estimate the heat capacity of certain other gases, and this estimate will be based upon such data as exist for these gases and upon analogies with the typical gases which have been considered above. These cases may best be considered as they occur in the later calculations.

THE DISSOCIATION OF TERNARY ELECTROLYTES.

By James W. McBain.

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The last paragraph of Part IV of A. A. Noyes and K. G. Falk's invaluable compilations of the more reliable data for the properties of aqueous electrolytes refers to the divergences in apparent dissociation of ternary electrolytes when the results of conductivity and freezing point measurements are compared without assuming other than the simplest possible ions; that is, assuming $Ba^{\cdot\cdot} + 2Cl'$, but not $BaCl^{\cdot}$ or $BaCl_3'$, etc.

They state:[1] "The most striking discordance between the two sets of ionization values is that presented by the bivalent metal halides, for which the values derived from the freezing point are always much larger than those derived from the conductance ratio. It has already been shown in Part II[2] of this series that the transference numbers of these substances are also abnormal, namely, in the respect that the cation transference decreases markedly with increasing concentration. There appears, however, to be no chemical explanation which would account for both of these anomalies, and it seems therefore probable that physical deviations must enter as a complicating factor."

It is the object of the present note to point out that the two phenomena occur in different ranges of concentration and that they are therefore in all probability due to separate causes. They may be explained in accordance with all other data by assuming intermediate ions (*e. g.*, $BaCl^{\cdot}$) in the more dilute, and complex anions (*e. g.*, $BaCl_3'$) in the more concentrated solutions, the effects of these ions being in opposite directions.

In 1905 the writer was interested in the question as to whether in complicated cases all the data with regard to mode and degree of ionization and the concentration and properties of the various molecular species present in a single aqueous solution could be quantitatively reconciled within the limits of the dissociation theory. To test this the extreme case of cadmium iodide and its potassium iodide derivatives was chosen,[3] since so detailed a comparison of the various methods for such cases did not appear to have been previously attempted. The result was very satisfactory from the standpoint of the dissociation theory, although for

[1] This Journal, **34**, 489 (1912).

[2] *Ibid.*, **33**, 1454–9 (1911).

[3] McBain, *Z. Elektrochem.*, **11**, 222 (1905).