The Variations of the Chemical Potential in Gas Mixtures with Density and Composition

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THE DENSITY AND COMPOSITION VARIATIONS OF CHEMICAL POTENTIALS IN GAS MIXTURES.

Introduction

In a thermodynamic study of isothermal equilibrium, the quantities of primary interest are the chemical potentials of the various substances present. The chemical potential was defined by Gibbs[1] through the energy differential for a system in which the masses are considered as independent variables. He writes

$$d\epsilon = t\,d\eta - p\,dv + \mu_1 dn_1 + \mu_2 dn_2 \quad \cdots\cdots \quad \mu_n dn_n \qquad (1)$$

for a system where ϵ is the energy of the system, t, p, and v the temperature pressure and volume, η its entropy, n_1, n_2 , etc. the amounts of substances one, two etc. present in the system, the units of which we shall take for convenience as mols, and μ_1, μ_2 etc. are the chemical potentials of the corresponding substances in the system. It follows readily from this definition and the definitions of the other thermodynamic functions that

$$\mu_1 = \left(\frac{\partial\epsilon}{\partial n_1}\right)_{\eta v} = \left(\frac{\partial\chi}{\partial n_1}\right)_{\eta p} = \left(\frac{\partial\Psi}{\partial n_1}\right)_{tv} = \left(\frac{\partial\zeta}{\partial n_1}\right)_{tp} \qquad (2)$$

where χ is the heat content, Ψ the Helmholtz free energy and ζ

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[1] Gibbs "Collected Works of J. Willard Gibbs", 1, 63. Longmans Green and Co., (1906) and (1928).

the Lewis free energy.

The usefulness of the chemical potential depends on the fact which can readily be proved thermodynamically that at equilibrium the chemical potential of a given substance must be equal throughout the system if a free transfer of the substance is possible between the various parts of the system, regardless of the state of aggregation of the various parts. Moreover, when a chemical reaction is possible in the system whose equation may be written as

$$aA + bB + ---- = cC + dD + ------- \qquad (3)$$

then at equilibrium an equation of the following form will hold for the chemical potentials.

$$a\mu_A + b\mu_B + ---- = c\mu_C + d\mu_D + ----- \qquad (4)$$

This expression is the mass action law in its rigorous form and requires a knowledge of the chemical potentials of the various constituents for its solution.

Since the chemical potential is of such importance, it is necessary to have some means of evaluating it as a function of the temperature, pressure or volume, and the various masses involved in the system. The isothermal variations of the chemical potential can be determined by means of various differential relationships. If we write the two free energy equations

$$d\Psi = -\eta dT - pdv + \mu_1 dn_1 + \mu_2 dn_2 \quad ----- \qquad (5)$$

$$d\xi = -\eta dT + vdp + \mu_1 d_1 + \mu_2 dn_2 \quad ------ \qquad (6)$$

then by cross differentiation we obtain

$$\left(\frac{\partial\mu_1}{\partial v}\right)_{Tn_1n_2--} = -\left(\frac{\partial p}{\partial n_1}\right)_{Tvn_2---}$$

and
$$\left(\frac{\partial\mu_1}{\partial p}\right)_{Tn_1n_2---} = \left(\frac{\partial v}{\partial n_1}\right)_{Tpn_2\ ---}$$

If therefore a function $F(T,p,v,n_1,n_2,\ ---) = 0$ is known, the chemical potential may be calculated except for an arbitrary temperature function. An equation of state for gas mixtures is of course such a function.

In the case of a gas, the fact that as the pressure approaches zero all gases approach the perfect gas in behavior, results in certain simplifications in the integration. For real gas mixtures we obtain, following Professor Beattie's[2] treatment, the following equations

$$\mu_1 = \int_V^\infty \left[\left(\frac{\partial p}{\partial n_1}\right)_{TVn_2} - \frac{RT}{V}\right] dV - RT \ln \frac{V}{n_1RT} + F_1' \qquad (9)$$

$$\mu_1 = \int_0^p \left[\left(\frac{\partial v}{\partial n_1}\right)_{Tpn_2} - \frac{RT}{p}\right] dp + RT \ln px_1 + F_1' \qquad (10)$$

R is the gas constant, x_1 the mol fraction of constituent one in the gas phase, and F_1' is a function of temperature only. It is frequently convenient in discussing the isothermal

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[2] Beattie, Phys. Rev., 31, 680, (1928).

variations of the chemical potential to discuss rather the fugacity, a function proposed by Lewis[3] and defined by the relation

$$\mu_1 = RT \ln f_1 + F_1' \qquad (11)$$

where f_1 is the fugacity of gas one. It can be seen that the fugacity contains no unknown temperature function yet describes completely the isothermal variation of the chemical potential with pressure or volume and composition.

There are a few simple rules which are frequently used for obtaining approximate results for chemical potentials in gas mixtures. The first is the simple form of Dalton's law which states that the equilibrium pressure of a gas in a mixture is equal to the total pressure times the mol fraction of that gas in the mixture. By equilibrium pressure is understood the pressure of the pure gas which would be in equilibrium with the mixture through a semipermeable membrane. Professor Gillespie[4] has shown that if this is true then the pure gases and the gas mixture obey the laws of Boyle and Avogadro. Consequently the gases are perfect gases and the integrals in equations (9) and (10) vanish, so that

$$\mu_1 = RT \ln px_1 + F_1' \qquad (12)$$

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[3] Lewis and Randall, "Thermodynamics", McGraw Hill Book Co., 191, (1923).

[4] Gillespie, Phys. Rev. 36, 121, (1930).

or, in terms of fugacities,

$$f_1 = px_1 \tag{13}$$

The second simple assumption is that made by Gibbs[5] and is frequently called the Gibbs form of Dalton's Law. This assumes nothing with regard to the equation of state of pure gases but requires additivity of pressures for gases on mixing. The assumption is that in a mixture a gas has the same value of the chemical potential that it has when pure and at the same concentration that it has in the mixture. This permits a substitution of the values of $\left(\frac{\partial p}{\partial n_1}\right)_{Tvn_2}$ for the pure gas in equation (9) and a solution for the chemical potential at the density equal to the density of gas one in the mixture.

The final simple rule that we shall consider here is the fugacity rule of Lewis and Randall.[6] This assumes that the fugacity of a component in a mixture is equal to the fugacity which that component would have if pure and at the total pressure of the gas mixture multiplied by the mol fraction in that mixture. In terms of chemical potentials this amounts to a simple substitution of $\left(\frac{\partial v}{\partial n_1}\right)_{Tpn_2}$ for the pure gas in integrating equation (10). All three of these rules are known to be inexact and the magnitudes of the errors will be discussed at a later point.

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[5] Gibbs. Loc. cit. p. 155.

[6] Lewis and Randall, Loc. cit. p. 226

II. METHODS OF EXPERIMENTAL MEASUREMENT

The previous discussion has indicated the two major methods of determining experimentally the isothermal variation of the chemical potential in gas mixtures. The first of these methods is what might essentially be called a comparison method. It depends on the property of the chemical potential of being equal throughout a system in equilibrium regardless of the phases in which the substance is present. It is necessary to confine oneself to comparatively simple systems in order to prevent the treatment from becoming so unwieldly that it is practically impossible to interpret the data except to use it as a test for some preconceived theory. For example it would be quite difficult if not impossible to obtain much information on the fugacities of nitrogen,hydrogen and ammonia in the ternary mixtures of the Haber equilibrium from data on that equilibrium. However. with some definite theory concerning the chemical potentials one can test the applicability of that theory as Professors Gillespie and Beattie[7] have done on the Haber equilibrium.

Simpler systems which present less difficulty are ones such as the vaporization of a liquid or solid into a gas or the dissociation of a solid giving a single gaseous dissociation product in contact with some other gas. Not only are the

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[7] Gillespie and Beattie. Phys. Rev. 36, 743,(1930).

results then much easier to interpret and easier to study but also they are more definite in disclosing failures of any proposed theory in that there is not the chance for so much compensation of errors when the theory is tested by the results.

Such simple systems have been studied by various workers, Pollitzer and Strebel[8], Larson and Black [9], Lurie and Gillespie[10], McHaffie[11], Euken and Bresler [12], and Braune and Strassman[13], In such cases it is usually a simple matter to calculate the change of chemical potential of the solid or liquid used due to the applied pressure and to the solution of gas in the liquid or solid providing it is not too soluble. The chemical potential in the gas phase of that component must of course at equilibrium be equal to that in the liquid or solid phase, and this the chemical potentials for the definite pressures and compositions experimentally obtained are thereby known. The calculations of the variations of the chemical potential of the liquid or solid proceed simply. The variation with the amount of dissolved gas will usually be sufficiently small in most cases so that a simple Raoult's law

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8. Pollitzer and Strebel, Zeits. fur Phys. Chem. <u>110</u>,786,(1924).
9. Larson and Black, J. Am.Chem.Soc.,<u>47</u>,1015, (1925).
10. Lurie and Gillespie, J. Am. Chem. Soc. <u>49</u>, 1146, (1927).
11. McHaffie, Phil.Mag. (7) <u>I</u>, 561, (1926).
    Phil.Mag. (7) <u>3</u>, 497, (1927).
12. Euken and Bresler, Zeits. f. Phys. Chem. <u>134</u>, 230, (1928).
13. Braune and Strassman, Zeits. f. Phys.Chem. <u>143 A</u> , 225,(1929)

correction will be sufficient. In fact in many cases - particularly in the case of solids - this correction may be neglected altogether. The variation with applied pressure may be calculated by equation (8). The resulting equation is:

$$\mu_1 - \mu_{1o} = \int_{p_o}^{p} \left(\frac{\partial v}{\partial n_1} \right)_{Tpn_2} dp + RT \ln y_1 \qquad (14).$$

where μ_1 is the desired chemical potential, μ_{10} the chemical potential of the liquid or solid when pure and under its own normal vapor pressure p_o at the temperature T, p is the total pressure, v the volume of the liquid or solid and y_1 the mol fraction of the liquid or solid in the liquid or solid phase. The final term is the Raoult's law correction. When the liquid or solid may be considered incompressible the equation reduces to a very simple formula which is frequently sufficiently accurate for the work in hand.

$$\mu_1 - \mu_{1o} = \left(\frac{\partial v}{\partial n_1} \right)_{Tpn_2} (p-p_o) + RT \ln y_1 \qquad (15)$$

One of the principal disadvantages of this method of measurement is that for a given liquid or solid phase and a single inert gas the system is divariant so that for a given temperature and pressure it is only possible to determine the chemical potential of a mixture of a single composition. This makes it impossible, unless one has a series of liquids and solids giving the same gaseous component at different chemical potentials - as for example a series of salt hydrates - to cover completely the possible pressure-composition range of the variation of the chemical potential.

The other principal method of attacking the problem experimentally is by means of equations (9) and (10), which are simply a more convenient form for gases of (7) and (8). The problem resolves itself into an experimental method of determining either $\left(\frac{\partial p}{\partial n_1}\right)_{Tvn_2--}$ or $\left(\frac{\partial v}{\partial n_1}\right)_{Tpn_2--}$. The methods heretofore used have been primarily to determine a function $F(p_1T_1v_1n_1n_2---) = 0$ from equation of state measurements and to obtain either analytically or graphically the desired derivatives and integrals from this source. The method usually employed is to determine an equation of state for each of the pure gases and by determining the way it varies between these two extremes by series of observations with certain mixtures of known proportions of the two gases. This method has been the most fruitful in determining the probable form of function that will satisfy the isothermal variations of the chemical potentials and its results will be dealt with more fully later.

The customary method of determining equations of state for mixtures given above becomes very difficult experimentally when one of the components is liquifiable at moderate pressures in the experimental temperature range. The required derivatives with respect to the number of mols of component are not the directly measured quantities but are obtained by a smoothing process between entirely different series of measurements. It seems possible and desirable to arrange the experimental procedure so that the required derivatives and integrals can be more directly obtained, with a probable increase of accuracy and a possibility of being able to work at lower temperatures in the case of condensible gases.

Consider equation (9). If we should set up our experiment in a constant volume container with a definite initial density of one gas and inject known amounts of the second gas we should obtain by measuring pressures a curve of pressure against the number of mols injected, whose derivative at any point would be $\left(\frac{\partial p}{\partial n_1}\right)_{Tvn_2}$ for the value of n_1 and n_2 in question. By obtaining series of such runs with different initial concentrations of the first gas, we could obtain the variation of $\left(\frac{\partial p}{\partial n_1}\right)_{Tvn_2}$ with the concentrations of both gases which could readily be integrated to give the desired integral for obtaining the chemical potentials.

Similarly by equation (10) we could vary the volume after an injection of the second gas, for example by injecting or extracting mercury from the system in sufficient quantity to hold the pressure constant and thereby measure the increase in volume on the addition of various numbers of mols of the second gas. In a manner similar to the previous case values of $\left(\frac{\partial v}{\partial n_1}\right)_{Tpn_2}$ and the resulting integral could be obtained.

These methods are considerably simplified experimentally under conditions where the gas to be injected can exist as a liquid under the conditions of temperature and pressure prevailing in the apparatus. Then it may be injected as the liquid and from its density and compressibility and the volume injected it is possible to calculate the number of mols injected. In order to evaporate the injected liquid in a reasonable length of time some sort of stirring is advisable. This type of measurement gives values of the chemical potential over the complete range of densities of both gases in contrast to the comparison method described above and the desired potentials may be very readily calculated from the data.

III. THE NATURE OF THE FUNCTION FROM EQUATION OF STATE CONSIDERATIONS

As has been previously mentioned, if we have an equation of state of the form $F(p,v,T,n_1n_2 \ldots\ldots) = 0$ for gas mixtures, it is possible to obtain directly values for the isothermal variation of the chemical potential by evaluating the integrals in equations (9) or (10). The choice of these equation~~s~~ depends on which set of independent variables is most convenient, v, t and n_1, n_2, or ptn_1n_2. Since numerous forms of equations of state have been proposed, some of which have received considerable experimental justification, it seems advisable to consider the nature of the integrals in equations (9) and (10) for gases following such equations.

Most of the equations of state proposed take the following form for a pure gas

$$p = \frac{n_1RT}{V} + \beta'\left(\frac{n_1}{V}\right)^2 \qquad (16)$$

or

$$\frac{V}{n_1} = \frac{RT}{p} + \beta \qquad (17)$$

where β and β' are functions of the temperature and density or pressure, consisting of a power series in the density or pressure and starting with a term independent of the density or pressure. The extent to which the series goes in the powers of the density or pressure depends on the particular equation under consideration.

It is to be expected that a gas mixture, provided no chemical reactions take place, will follow the same sort of equation except that for n_1 will be written the summation $\lesssim n_1$ of the components and the β's will be functions of the composition as well as the temperature and density or pressure. These composition functions must be if course such that as the composition of the mixture approaches that of either pure gas the β of the mixture will approach that of the pure gas.

It can readily be shown that if equations (16) and (17) are valid there is a simple relation between the β and β' and we may write for gas mixtures:

$$p = \frac{\lesssim n_1 RT}{V} + RT\beta_{om}\left(\frac{\lesssim n_1}{V}\right)^2 + \text{higher terms in } \frac{\lesssim n_1}{V} \qquad (18)$$

$$\frac{V}{\lesssim n_1} = \frac{RT}{p} + \beta_{om} + \text{higher terms in} \frac{\lesssim n_1}{V} \text{ or } p \qquad (19)$$

Since the higher terms in the case particularly of mixtures are quite uncertain, especially as to their variation with composition, it will suffice here to discuss the simple case where the higher terms are neglected and the β_{om}'s are purely functions of the temperature and composition. General considerations from experiment and statistical mechanics indicate[14] that β_{om} should behave in such a manner in relation to the β's of the two pure gases making up the mixture that

$$\beta_{om} = \beta_{o1}x_1^2 + 2\beta_{o12}\, x_1 x_2 + \beta_{o2}x_2^2 \qquad (20)$$

where x_1 and x_2 are the mol fractions of gases 1 and 2 respect-

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[14] See for example Beattie and Ikehara, Proc.Am.Acad.Arts Sci. 64, 127, (1930).

ively and β_{01} and β_{02} are the β functions for those pure gases. β_{012} is an interaction function, dependent only on the temperature and the two gases under consideration.

In making this substitution in equations (18) and (19) and solving equations (9) and (10) respectively for the values of the chemical potential one obtains

$$\mu_1 = -RT \ln \frac{V}{n_1RT} + 2\beta_{01} \frac{n_1RT}{V} + 2\beta_{012} \frac{n_2RT}{V} + F_1' \qquad (21)$$

$$\mu_1 = RT \ln px_1 + \beta_{01}p - (\beta_{01} + \beta_{02} - 2\beta_{012})\, px_2^2 + F_1' \qquad (22)$$

These equations, because of neglecting higher powers of $\frac{\Sigma n_1}{v}$ and p, are limited in validity to low pressures or densities but in many cases the effect of the higher terms is negligible within the experimental error up to quite appreciable pressures, as will be shown more fully later.

One of the forms of equation of state which has met with considerable experimental justification is that of Beattie and Bridgeman.[15] In this equation β_0 is of the form

$$\beta_0 = B_0 - \frac{A_0}{RT} - \frac{C}{T^3} \qquad (23)$$

where B_0, A_0 and C are constants dependent on the nature of the gas. In applying this to mixtures it is found advisable to

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[15] Beattie and Bridgeman, Proc. Am. Acad. Arts Sci. 63, 229(1928)
J. Am. Chem. Soc. 50, 3133. (1928).
Zeitsh. f. Physik 62, 95, (1930).

combine individual constants according to the method of equation (20) in order to determine the interaction constants from those of the pure gases. The interaction constant for the B_0's is $1/2\ (B_{01} + B_{02})$, that for the A_0's is $(A_{01}A_{02})^{1/2}$ and similarly for the C's, $(C_1C_2)^{1/2}$. For this method of combination therefore β_{012} becomes

$$\beta_{012} = \frac{1}{2}(B_{01} + B_{02}) - \frac{(A_{01}A_{02})^{\frac{1}{2}}}{RT} - \frac{(C_1C_2)^{\frac{1}{2}}}{T^3} \tag{24}$$

Where the equation of state for the pure gases is known the uncertainty in the determination of chemical potentials in mixtures comes primarily in this β_{012} term and consequently it will be advantageous to study it more fully at a later point. There results for this particular treatment of the equation of state consequently:

$$\mu_1 = -RT \ln \frac{V}{n_1RT} + 2\left[B_{01} - \frac{A_{01}}{RT} - \frac{C_1}{T^3}\right]\frac{n_1RT}{V} + \left[B_{01} + B_{02} - \frac{2A_{01}^{\frac{1}{2}}A_{02}^{\frac{1}{2}}}{RT} - \frac{2C_1^{\frac{1}{2}}C_2^{\frac{1}{2}}}{T^3}\right]\frac{n_2RT}{V} + F_1' \tag{25}$$

$$\mu_1 = RT \ln px_1 + \left[B_{01} - \frac{A_{01}}{RT} - \frac{C_1}{T^3}\right]p + \left[\frac{(A_{01}^{\frac{1}{2}} - A_{02}^{\frac{1}{2}})^2}{RT} + \frac{(C_1^{\frac{1}{2}} - C_2^{\frac{1}{2}})^2}{T^3}\right]px_2^2 + F_1' \tag{26}$$

These methods of combining B and A were tried years ago in connection with the Van der Waals' equation of state with moderate success. Application to the β and A of the Keyes equation gave good results when applied to the data of Keyes and Burks[16] and of Lurie and Gillespie[10].

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[16] Keyes, J. Am. Chem. Soc. 49, 1393 (1927).
Keyes and Burks, J. Am. Chem. Soc. 50, 1100, (1928).

Beattie and Ikehara used these methods for B_0 and A_0, but they used a different method of combination for C's, the present method having since been found necessary by Dr. Eli Lurie and by others working in this laboratory.

These equations indicate the general nature of the deviations to be expected from the perfect gas law in the treatment of the chemical potentials of gas mixtures. It will be of interest to take these derived forms and to see if it is possible by their use to treat the data of Braune and Strassman on mixtures of iodine with carbon dioxide and hydrogen and to see if it is possible thereby to derive equation of state constants for iodine which will satisfactorily describe the behavior of the chemical potential of iodine vapor mixed with various inert gases.

IV. APPLICATION OF THE PREVIOUS METHODS TO COMPARISON MEASUREMENTS.

In the use of the comparison method for studying the chemical potentials of gas mixtures where a liquid or solid is equilibrated with the gas mixture, the experimental variables are usually pressure, temperature and mol fractions rather than the densities, which for gases are quite difficult to measure, particularly in this type of procedure. Consequently we shall use equations (22) and (26) in treating this case. We shall treat the case where equation (15) is applicable and for μ_{1o} we shall substitute the value for the pure gas so that equation (15) reduces to the following form:

$$\mu_1 = RT \ln p_o + \beta_{o1} p_o + \left(\frac{\partial V}{\partial n_1}\right)_{Tpn_2} (p-p_o) + RT \ln y_1 + F_1' \qquad (27)$$

By equating this potential with that for the gas mixture-which is equal if equilibrium has been obtained - the result is obtained:

$$RT \ln \frac{p_o}{px_1} + RT \ln y_1 = \left[\beta_{o1} - \left(\frac{\partial V}{\partial n_1}\right)\right](p-p_o) - (\beta_{o1}+\beta_{o2}-2\beta_{o12})px_2^2 \qquad (28)$$

In the usual case where the liquid or solid directly vaporizes the quantity $\left(\frac{\partial V}{\partial n_1}\right)$ is the molal volume of the liquid or solid. If the equations if state of the two pure gases and the normal vapor pressure of the liquid or solid are known it then is a simple matter to calculate the β_{o12} of the gas mixture under consideration from the experimental data. This would be a very fertile way of studying the methods of combination of constants for gas mixtures in cases where the equations of state for the pure substances are known. In fact values of p_0 would not be necessary if experiments were carried out over a range of pressures at each temperature considered. However, in most of the cases where data are at present available this particular way of studying the chemical potential in gas mixtures is impossible due to the fact that the equation of state for the pure vapor is not known.

Such cases require the solution for β_{01} as well as β_{012} . (β_{02} will generally be known for most of the gases used for a second gas[15]) In order to be able to do this it is necessary to assume a form for β_{01} and β_{012} as was done in equation (26) and to see if it is possible to obtain constants for the equation of state for mixtures expressed in a definite form which will satisfactorily fit the data.

This method will in general require the following data: -

1. Values of p and the corresponding mol fractions in the gas over the desired temperature range with the given liquid or solid in equilibrium with two different gases whose equation of state constants are known. These data need only be for one value of the pressure in each gas provided the pressures used are the same at any given temperature. These data should in general be of greater accuracy than the subsequent data and can usually be best obtained under the usual

experimental conditions at pressures around one atmosphere. The inert gases chosen should preferably be two whose equation of state constants are as different as possible.

(2) Values of p and the corresponding mol fractions for various values of the pressure, with one of the two inert gases used above, at certain temperatures covering the desired temperature range.

(3) Values of the molal volume of the liquid or solid and the solubility of the inert gases used over the temperature range in question. Since the corrections from this source are in general small the accuracy required is not very great.

If the available data were of extraordinary accuracy and we could count implicitely on the form of the temperature function in equations (23) and (24) then data listed under heading 2 and 3 would suffice to determine the equation of state constants and consequently the chemical potentials in gas mixtures. In practice, however, the additional data under heading 1 must be used to give further aid in their determination. This results from the fact that in equation (28) the coefficient of $p-p_0$ depends only on the liquid or solid and its pure vapor and is consequently independent of the inert gas used. Information on the coefficient of the second term may consequently be obtained by the comparison of data with different inert gases such as that under heading 1.

For the case under consideration the Beattie-Bridgeman form of equation of state combined with equation (28) gives

$$RT \ln \frac{p_0}{px_1} + RT \ln y_1 = \left[B_{01} - \frac{A_{01}}{RT} - \frac{c_1}{T^3} - \frac{\partial V}{\partial n_1}\right](p - p_0) + \left[\frac{(A_{01}^{\frac{1}{2}} - A_{02}^{\frac{1}{2}})^2}{RT} + \frac{(c_1^{\frac{1}{2}} - c_2^{\frac{1}{2}})^2}{T^3}\right] p x_2^2 \qquad (29)$$

Now at a given temperature and pressure the first term can be eliminated by means of measurements with two different inert gases. There results, using the asterisk to designate values for the second inert gas,

$$\frac{(RT)^2}{p}\left[\ln \frac{x_1^*}{x_1} - \ln \frac{y_1^*}{y_1}\right] = (A_{01}^{\frac{1}{2}} - A_{02}^{\frac{1}{2}})^2 x_2^2 - (A_{01}^{\frac{1}{2}} - A_{02}^{*\frac{1}{2}})^2 x_2^{*2} + R\,\frac{(c_1^{\frac{1}{2}} - c_2^{\frac{1}{2}})^2 x_2^2 - (c_1^{\frac{1}{2}} - c_2^{*\frac{1}{2}})^2 x_2^{*2}}{T^2} \qquad (30)$$

In almost every case where p_0 is low (which is usually the case for this type of experiment) x_2^2 and x_2^2 will differ so slightly that an average value may be used in the right-hand side of the equation thus reducing it to

$$\left[2A_{01}^{\frac{1}{2}}(A_{02}^{*\frac{1}{2}} - A_{02}^{\frac{1}{2}}) + A_{02} - A_{02}^* + R\,\frac{2c_1^{\frac{1}{2}}(c_2^{*\frac{1}{2}} - c_2^{\frac{1}{2}}) + c_2 - c_2^*}{T^2}\right]\bar{x}_2^2 = M\bar{x}_2^2 \qquad (31)$$

If values of M are calculated from the experimental measurements, and are plotted against $\frac{1}{T^2}$ a line will result whose intercept determines A_{01} and whose slope determines C_1. The normal experimental errors are such that the slope will seldom be determined very accurately and it usually must be readjusted after a consideration of the variable pressure data.

Using the approximate values of A_{01} and C_1 found in this way a value of B_{01} can be calculated from applying equation (29) to the variable pressure data at each temperature. This, it can readily be seen, does not require any knowledge of p_0 and thus a value of B_{01} is obtained at each temperature. Unless the values of A_{01} and C_1 chosen are correct the value of B_{01} with temperature will show a trend. This means that the line drawn on the M, $1/T^2$ plot must be readjusted in slope and new values of A_{01} and C_1 obtained. Usually if B_{01} decreases as the temperature increases it indicates that the C_1 value and consequently the slope chosen was too large. This readjustment is carried on until the deviations on the M, $1/T^2$ plot are not excessive and a satisfactory constancy of B_{01} with temperature is obtained.

The final values of A_{01} , B_{01} and C_1 thus obtained may then be used for the calculation of chemical potentials in the gas mixtures of the vapor with various inert gases, or by equation (29) they may be used to obtain good values of the normal vapor pressure p_0 from the best experimental measurements, They can probably justifiably be used in determining the equation of state of the pure vapor by the use of equations (18) or (19) and (23). The accuracy of these corrections on the perfect gas law will probably be considerably less when so used than when the constants are used to calculate corrections on the same type of data from which they were determined; but, in many cases, such as that of iodine which we are about to discuss, there is little probability of being able to determine the equation of state with equal accuracy by direct measurement.

The treatment proposed here has recently been published[16] and is presented here from a somewhat different point of view with but minor changes and improvements,

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[16] Gerry and Gillespie, Phys. Rev. 40, 269, (1932)

V. APPLICATION TO IODINE VAPOR.

Practically the only substance for which suitable data exist at present for the application of this method is Iodine. Braune and Strassman[13] have recently published data from which the variation of px_1 from one atmosphere to about forty atmospheres with carbon dioxide could be calculated over a temperature range of about 60°C. They also give observations at one atmosphere with both carbon dioxide and hydrogen as inert gases. Due to a lack of smoothness of their results as a function of temperature the best results for normal vapor pressures will probably be obtained by correcting the results of Baxter, Hickey and Holmes[17] and of Baxter and Grose[18] who used air as an inert gas. However, the use of a different gas for the determination of vapor pressures from either of those used in determining the constants introduces a certain possibility of greater error in the calculation of the corrections, as will be discussed more fully later.

Unfortunately Braune and Strassman do not give their direct experimental quantities but calculated values, which fact necessitates a reversal of their calculations to get their experimental variables p and x_1. At ten temperatures they give values at one atmosphere for hydrogen and carbon dioxide. Three of these are sufficiently inconsistent to fall off the plot in Figure 1 where the quantity M of

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[17] Baxter, Hickey and Holmes, J. Am. Chem. Soc. 29, 127, (1907)

[18] Baxter and Grose, J. Am. Chem. Soc. 37 , 1061, (1915).

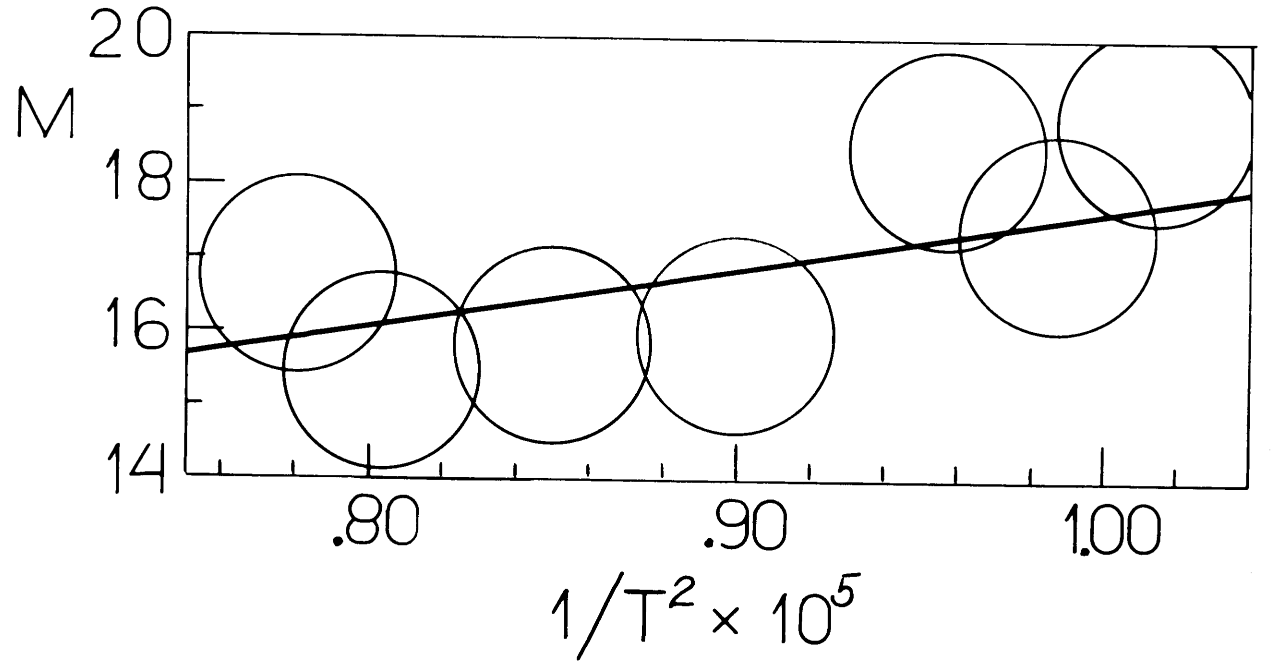

Fig. I

equation (31) is plotted against $1/T^2$. The radii of the circles correspond to an accumulated error of 0.2 percent on their combined results for hydrogen and carbon dioxide at the temperature in question. The line corresponds to the final values of A_{01} and C_1 chosen after obtaining a proper value of B_{01} as described above.

The values of the constants found for iodine are given in Table 1. Carbon dioxide and hydrogen were assumed insoluble in solid iodine and the International Critical Tables[19] values for the density of solid iodine were used. The deviations in percent of the observed values of the quantity $\frac{px_1}{p_0}$ in the high pressure observations with carbon dioxide from the values calculated by equation (29) using these constants are shown in Figure II. The circles correspond to the claimed experimental accuracy of the measurements.

TABLE I

Values of the constants for iodine vapor in the Beattie-Bridgeman equation of state for low pressures. Units: atmospheres, liters, moles, $T = t^\circ C + 273.13$.

Constant	A_{01}	B_{01}	C_1	R	Molecular Weight
Value	17.0	0.325	4000×10^4	0.08206	253.864

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[19] International Critical Tables, 21 (1928).

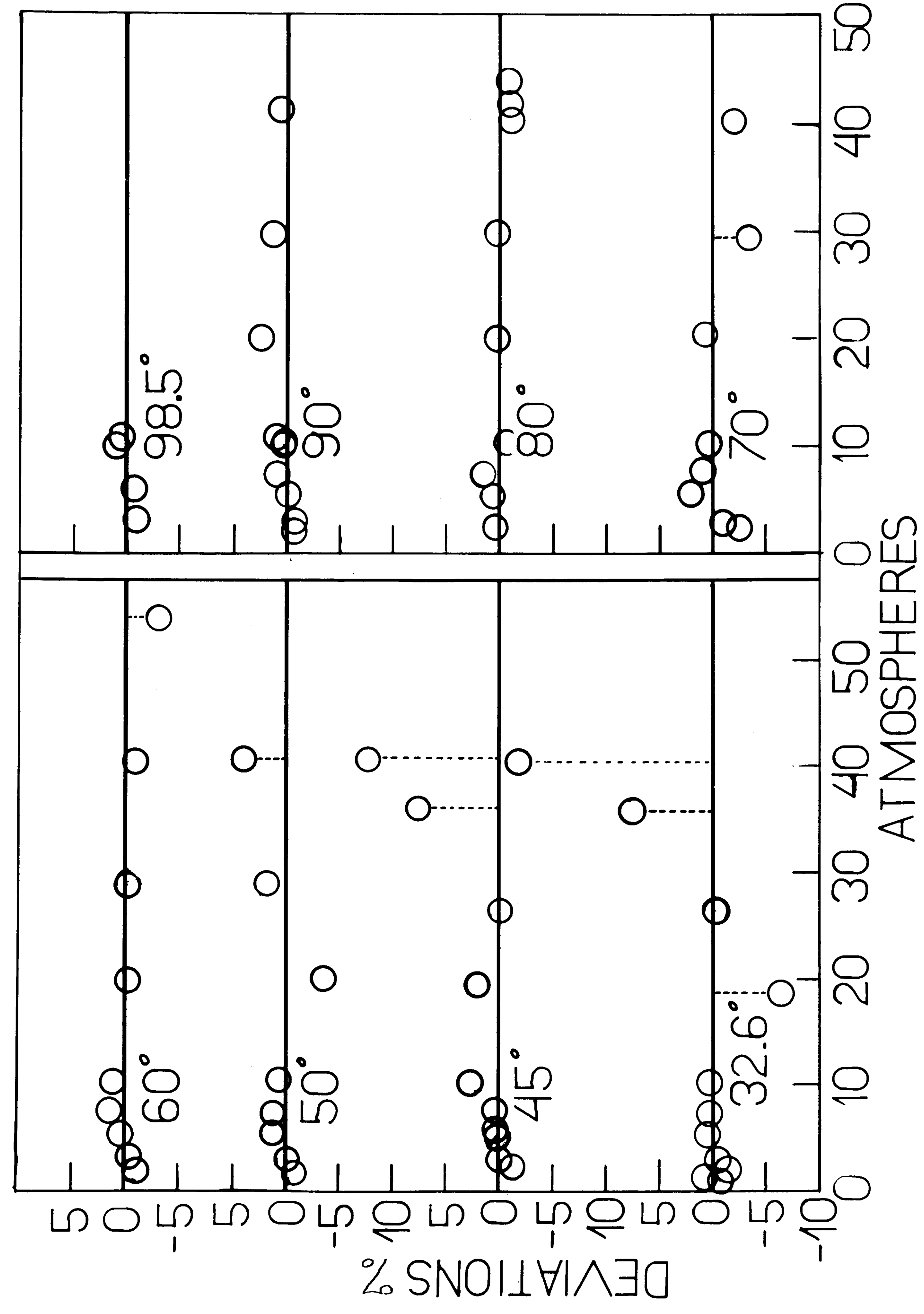
DEVIATIONS %
ATMOSPHERES
5
0
-5
5
0
-5
-10
5
0
-5
-10
5
0
-5
-10
0
10
20
30
40
50
0
10
20
30
40
50
60°
50°
45°
32.6°
98.5°
90°
80°
70°

Fig 2

It can be seen that the deviations are not systematic from temperature to temperature except possibly for the low temperature higher pressure points where we might well expect the low pressure equation we are using to be insufficient, since the magnitude of px_1 is about twice p_0.

Since the one-atmosphere observations are probably more exact than those at higher pressures, the one-atmosphere points were used to calculate the normal vapor pressure of iodine with the aid of the above constants. For the purpose of showing the importance of the corrections, the values of px_1 as well as the normal vapor pressures obtained from them are given in Table II, together with the best values from the high pressure carbon dioxide experiments.

TABLE II

Values of px_1 at one atmosphere and normal vapor pressures of iodine in millimeters of mercury.

				Normal Vapor Pressures		
t^oC	px_1CO_2	px_1H_2	High p CO_2	p_oCO_2 1 atm.	p_oH_2 1 atm.	Aver. of last two.
32.6	.5778	.5608	.5687	.5642	.5635	.5639
45.0	1.504	1.467	1.482	1.473	1.474	1.4735
50.0	2.243	2.185	2.207	2.199	2.196	2.197
60.0	4.281	4.191	4.244	4.206	4.211	4.208
70.0	8.254	8.095	8.185	8.124	8.131	8.127
80.0	15.23	14.96	15.14	15.01	15.02	15.015
85.0	21.20	20.82	---	20.91	20.90	20.90

A comparison of the px_1 values with the corrected values of the vapor pressure shows that the corrections are quite significant and bring about a much better agreement between the two sets of data.

The normal vapor pressures calculated from the data of Braune and Strassman are found not to be smooth when their logarithms are plotted against 1/T. This is however true of the original observations.

Some experiments by Baxter and his co-workers[17,18] wherein dry carbon dioxide free air at one atmosphere was equilibrated with iodine in order to determine the vapor pressure of iodine, appear very accurate. The vapor pressures are a smooth function of the temperature.

The algebra of combination of constants is such[20] that a mixture such as air, where the constituents always appear in the same proportions, may without any inconsistency be treated as a pure substance in applying the equations here presented. The values of the constants may be either determined experimentally from equation of state measurements or by combining constants for the component gases. Those we shall use were determined directly[15]. By the use of these constants with those derived for iodine we can calculate the necessary corrections to obtain normal vapor pressures,

The number of mols of air in their experiments was obtained by measuring the volume of wet air over water and assuming that the volume of dry air may be calculated by the customary procedure involving the ideal gas laws. This

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[20] Gillespie, Phys. Rev. <u>34</u>, 1605, (1929).

assumption is in general much better at low pressures than would at first appear obvious, due to a large degree of compensation of errors under the particular conditions used.

Using this assumption Baxter and co-workers find for one atmosphere total pressure with air as the inert gas the following equation to fit their experimental points:

$$\log px_1 = 9.7522 - \frac{2863.54}{273 + t^{\circ} - 19} \qquad (32)$$

With the aid of equation (29) and the assumption that air is insoluble in solid iodine, values of the normal vapor pressure of iodine have now been calculated from the date of equation (32) for even values of the temperature. These are given in Table III together with the corresponding values of px_1.

TABLE III

Values of px_1 and of the normal vapor pressure of iodine in millimeters of mercury according to the measurements of Baxter and collaborators by the gas current method.

$t^{\circ}C$	0	10	20	30	40	50	60	70	80	90	100
px_1	0.03009	0.0804	0.2001	0.4670	1.0287	2.1511	4.292	8.206	15.092	26.79	46.04
p_0	0.02981	0.0798	0.1988	0.4643	1.0235	2.1419	4.276	8.179	15.047	26.71	45.89

These p_o values are in fair agreement with those from Braune and Strassman's measurements if one considers the lack of smoothness of the latter. The average deviation between the two is about a percent and a half. It can be noticed from the last two tables that the deviations from ideality are important even at as low pressures as one atmosphere.

Giauque[21] has recently smoothed the data of Baxter and his co-workers with the aid of spectroscopic and specific heat data. Application of his method to the corrected results of Baxter gives an equation which fits the data well within the probable experimental accuracy. This equation is

$$\log p_{o_{\text{atm.}}} = - \frac{3512.8}{273.1+t^o} - 2.013 \log (273.1 + t^o) + 13.3740 \quad (33)$$

Due to the theoretical advantages of this form, the vapor pressures calculated from it are probably more accurate than those given in Table III using Baxter's empirical smoothing function. The coefficient of the reciprocal absolute temperature is the only constant which differs numerically from that used by Giauque as the other constants were derived by him from specific heat and spectroscopic data. The agreement of equation (33) with the data is slightly better than that of the empirical equation (32).

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[21] Giauque, J. Am. Chem. Soc. 53, 507, (1931).

VI. A COMPARISON OF METHODS OF CALCULATION.

In order to consider the magnitude of the errors made by assuming simple relations for the chemical potentials it will be well to calculate the errors that would be made in the case of iodine by means of the constants we have derived.

The simple form of Dalton's law states that the equilibrium pressure of a gas in a mixture is equal to the total pressure times the mol fraction of that gas in the mixture. The data that have already been presented indicate the failure of this law although not the exact extent as the comparison of px_1 with p_0 also includes the effect of pressure on the vapor pressure. Using the equation for the chemical potential of a pure gas at the equilibrium pressure and equating that potential to that of the mixture given in equation (26) we obtain the equation:

$$RT \ln \frac{p_1}{px_1} = \left[B_{01} - \frac{A_{01}}{RT} - \frac{c_1}{T^3}\right](p-p_1) + \left[\frac{(A_{01}^{\frac{1}{2}} - A_{02}^{\frac{1}{2}})^2}{RT} + \frac{(c_1^{\frac{1}{2}} - c_2^{\frac{1}{2}})^2}{T^3}\right]px_2^2 \qquad (34)$$

The deviation of $\frac{px_1}{p_1}$ from unity gives the deviation from this simple form of Dalton's law.

The Gibbs form of Dalton's law, that the chemical potential of a gas in a mixture is the same as that of a pure gas at the same density which that component has in the mixture, is known to be inexact, but it has been found in many of the cases studied[4] that the results obtained were superior to the previously mentioned form of Dalton's law. This is not necessarily the case as can readily be seen by studying the identity.

$$\frac{px_1}{p_1} \Bigg/ \left[\frac{n_{1m}}{V_m} \Big/ \frac{n_1}{V_1}\right] = \frac{pV_m}{\Sigma n_{1m}} \Bigg/ \frac{p_1V_1}{n_1} \qquad (35)$$

This equation gives a simple means of calculating these deviations from the previously calculated values of $\frac{px_1}{p_1}$ as $n_{1m}/V_m \Big/ \frac{n_1}{v_1}$ gives by its difference from unity the deviation from this rule.

The fugacity rule of Lewis and Randall is another method of calculating equilibrium pressures. According to this rule the value of $\frac{px_1}{p_1}$ should be given as follows

$$RT \ln \frac{p_1}{px_1} = \left[B_{01} - \frac{A_{01}}{RT} - \frac{C_1}{T^3}\right] (p-p_1) \qquad (36)$$

The difference of the value of p_1 thus obtained from the true value given by equation (34) measures the amount of error of this rule.

By these methods we have calculated the deviations in percent from these simple rules at conditions of saturation at one atmosphere total pressure in three different inert gases at two temperatures. These are given in Table IV and it will be noticed that in all cases the deviations are important compared with the possible experimental accuracy.

Table IV

Deviations in percent of the simple rules for calculating equilibrium pressures for iodine in various inert gases.

Inert Gas	Air		Hydrogen		Carbon Dioxide	
t°C	25	75	25	75	25	75
$100\frac{n_{1m}}{V_m}-\frac{n_1}{V_1}\frac{n_1}{V_1}$	.45	.07	-.77	-.73	2.95	1.57
$100\frac{px_1-p_1}{p_1}$	.42	.13	-.71	-.61	2.43	1.31
Fugacity rule	7.5	4.2	8.7	5.0	5.5	3.0

It can be seen that the deviations from the Gibbs-Dalton law are of the same order of magnitude and in general slightly greater than for the simple rule. This is in general what we would expect from equation (35) in the case of small mol fractions where p is much greater than p_1 as is usually the case in this type of measurement. It can also be seen that the fugacity rule is extremely bad for cases of condensible substances at small mol fractions.

In the case of the determinations of vapor pressures graphical extrapolations are sometimes used. For example one can extrapolate values of px_1 for various values of p to the limit where p equals po. There is here, however, an uncertainty due to the dependence of the corrections on the two variables p and x which vary simultaneously. A rapid change of x with p takes place as p approaches po below the values of p usually worked with in such measurements. From the general nature of the function of equation (28) we should be led to expect a curve of the general nature of Fig. III. A graphical extrapolation such as is indicated by the dotted line would not pass through the origin and would cause an error thereby. This error will usually be negligible only when the vapor pressure is less than three or four millimeters judging by the case of iodine.

Extrapolation of the quantity $\frac{n_{1m}}{V_m}$ against the density of inert gas offers theoretical advantages in that the extrapolation should be more nearly linear. However, due to the fact that almost always the experimental variables are pressures rather than densities the transposition to densities without an equation of state for the mixtures would introduce uncertainties equal to or greater than those of the px, extrapolation. Consequently graphical methods are not satisfactory for the case of determination of vapor pressures.

The method we have used here is suitable, and should prove quite useful, for the determination of normal vapor pressures by the gas current method as we have done in the case of iodine. Its applicability is quite general, and its accuracy quite good.

In the case where the available variable pressure data are with the same inert gas as the best one-atmosphere data from which the normal vapor pressures are to be determined,

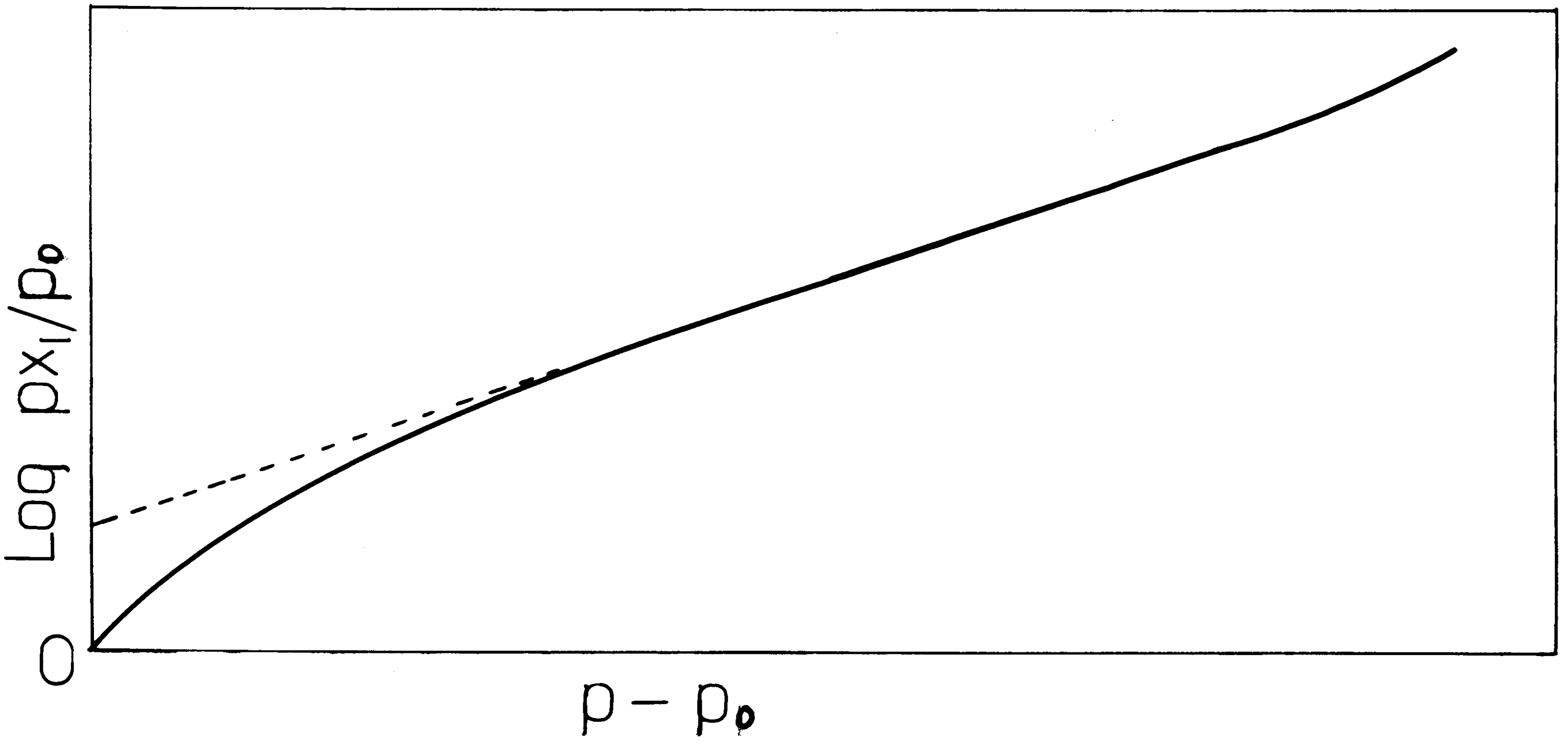

Fig III

the method proposed can be regarded simply as a means of determining the amount of curvature at low pressures, illustrated in Fig. III for a single isotherm, and of smoothing the corrections as a function of the temperature. Under these circumstances we should expect very precise results in the determination of the normal vapor pressures over the experimental temperature range.

Where the corrections are applied to data with a different inert gas from either of those used in determining the constants of the equation, the possibilities of erro are multiplied. We have applied it above in this way in the case of the iodine-air work of Baxter and his collaborators. In a case such as this, particularly as the corrections are intermediate between those for the two inert gases used in determining the constants, it seems entirely probable that the corrections are of the right order of magnitude though probably of considerably less accuracy than those calculated for carbon dioxide. The uncertainties of the method as a whole appear in any event to be less than those of the other methods used for the calculation of normal vapor pressures from data of the gas current method.

VII. FIRST APPARATUS FOR THE DETERMINATION OF THE CHEMICAL POTENTIAL.

In an earlier section a new method of evaluating the isothermal variation of the chemical potential has been described. The novelty depends on the arrangement of the experimental procedure for taking equation of state data of mixtures in such a manner that the differential

can be directly evaluated from the data. The proposal is to have a constant volume container into which known amounts of a vaporizable liquid can be injected and the pressure increase measured after evaporation of the liquid.

An apparatus has been constructed on these principles, and has been applied to the problem of determining the chemical potential of water in gaseous mixtures with carbon dioxide. It was found by experiment that in capillaries of less than about five hundredths of a millimeter diameter that evaporation back down the capillary was extremely slow, even at elevated temperatures as long as the external pressure was kept well above the vapor pressure of water. Capillaries could be constructed so that the evaporation back into the capillary was much less than a millimeter in several hours. Consequently it was considered feasible to use such a fine capillary for injecting water into the bomb, as during the time of measurement the water ejected from the capillary would be evaporated, while that in the capillary would not evaporate appreciably. In order to obtain evaporation, and a homogeneous gas mixture in a reasonable length of time a stirrer was introduced. To prevent possibilities of leakage the stirrer was constructed to be entirely within the bomb, and to be operated by a magnetic field from magnets outside the bomb. The stirrer was of the propellor type, designed to circulate the gas in the bomb over the capillary. In order to ascertain the position of the meniscus in the capillary, and to observe the evaporation of the liquid from the outside of the capillary as well as to check up on the proper operation of the stirrer, two windows were introduced in the bomb.

The details of the construction of the bomb, and its connections to the various other parts of the system are illustrated in Fig. IV. The bomb C is made of four-inch heavy walled brass tubing about ten inches long. The two caps, machined out of solid brass, are screwed on and soldered to make them gas-tight. The stirrer B consists of a brass propeller mounted on a shaft with a soft iron armature on the upper end at J. This armature, which was copper plated and then silver plated to prevent corrosion, rotates in a cylindrical projection in the center of the upper cap to the bomb. Over the outside of this cylinder a group of six electromagnets can be fitted. These are connected to a motor

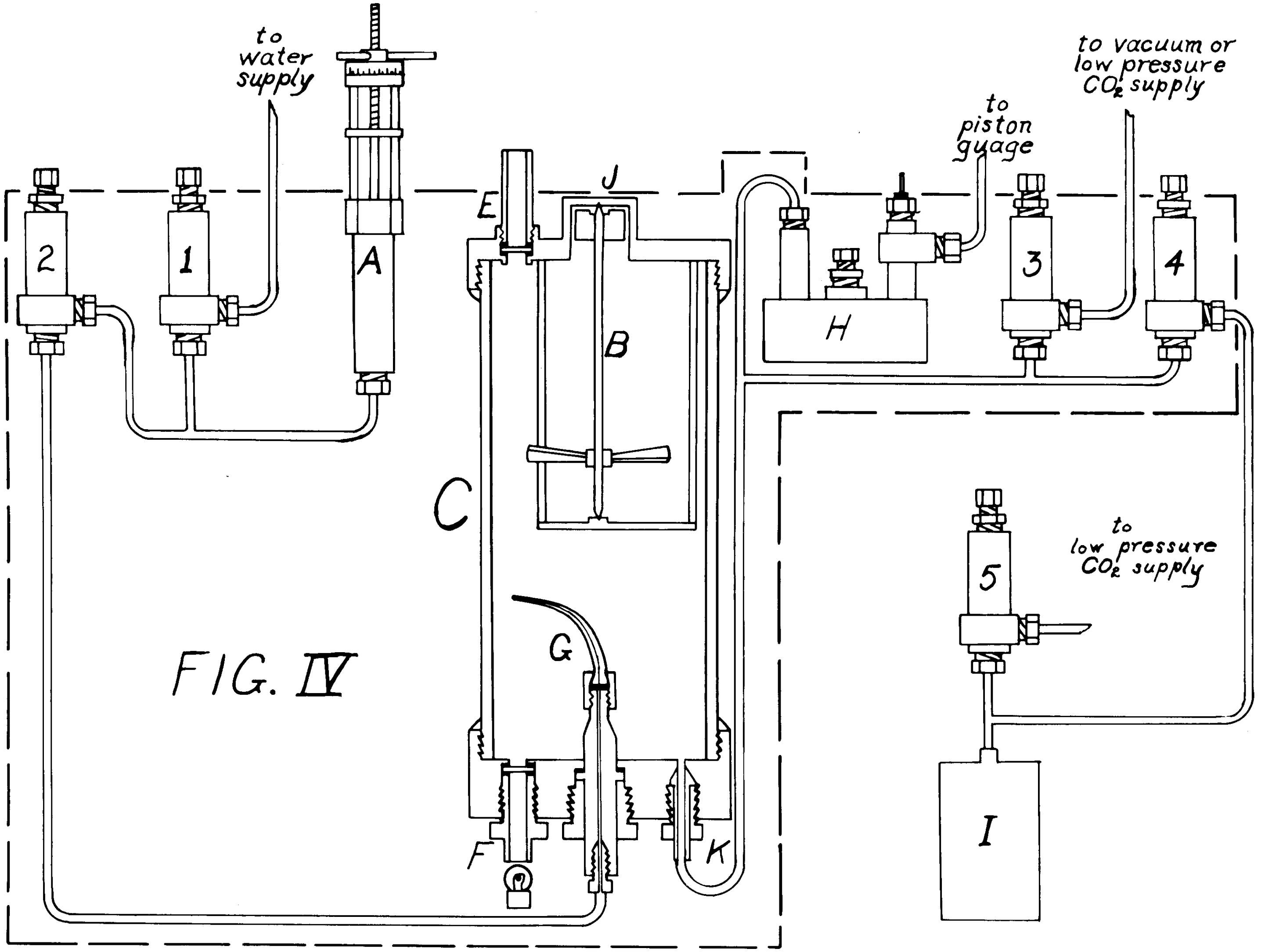

DIAGRAM OF APPARATUS

driven commutator in such a way as to give a rotating magnetic field which drags the armature around with it, thus driving the stirrer.

Two round glass windows cut from thick plate glass and 3/8" in diameter were placed one in each cap of the bomb at E and F. These were made gas-tight by screwing them in with lead washers. Below the lower window at F, a small six-volt light was placed, and the upper window was protected by a brass tube three inches long from the thermostat oil in which the bomb was to be placed. These windows were so placed that the ends of the stirrer blades could be seen when it rotated. At the bottom of the bomb at G a fine glass capillary with heavy walls,such as was described above, was attached to a brass coupling by screwing down on a lead washer on a ground glass,brass connection. This coupling passed to the outside of the bomb where a copper tube to a water supply could be connected by a cone joint. The end of the glass capillary was bent over so that the end came between the two windows. A cone joint at K provided a connection for a copper tube leading to the pressure measuring device and loading apparatus.

The method used to measure the amount of water forced through the capillary was to use a small piston screw injector A of the type customarily in use in this laboratory.

The diameter of the piston was 0.22 in and a one-millimeter thread was used for the screw. The total capacity of the injector was about 1.8 cc. The rotating unit was marked to read directly to hundredths of a turn, and thousandths could be readily estimated. One complete turn of the unit corresponded to a volume ejected of about 1/40 cc. The piston and cylinder were made from turbine steel, a stainless steel. This injector was connected to the glass capillary of the bomb through copper tubes, and a steel stopcock 2 which was introduced to facilitate loading of the injector with water. A second steel stopcork 2 was provided in this line for loading from which a copper tube ran to the water supply. All the stopcocks used were of the type customarily used in this laboratory, but made with pistons and cylinders of turbine steel to prevent corrosion. The stopcocks and injector were packed with a graphite-impregnated asbestos twine which was found to be the most suitable packing for resisting the temperatures and pressures used.

Connection K from the bomb led to a turbine steel riser block H which is essentially a mercury U tube with a steel stopcock between the two arms. The arm away from the gas connection was filled with oil above the mercury surface, and the oil was connected by a steel tube to a piston pressure guage. In this arm there was also a insulated steel needle by which one could detect electrically when the two arms of the U tube were balanced. The method used in this point of the work was simply to connect this contact and the U tube in series with a telephone, and the two volt connections of a transformer.

The piston guage was of the type customarily used in this laboratory for measuring pressures accurately. The constant of the piston used was of such a magnitude that one gram on the guage was approximately equal to one millimeter pressure, and the guage was sensitive to about a tenth of a gram. The construction of these guages has been elsewhere described.[22]

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[22] Keyes and Brownlee, J. Am. Chem. Soc. 40, 25, (1918).
Keyes and Dewey, J. Opt. Soc. Am. 14, 491, (1927).
Beattie and Edel, Ann. der. phys. 11, 633, (1931).

To this connecting tube K are also connected two stopcorks of turbine steel. One of these passes directly to a glass system for evacuation, or low pressure carbon dioxide supply. The other is connected to a steel storage bomb I of about fifty cc. capacity which can be loaded through an ordinary steel stopcock (5) with liquid carbon dioxide by cooling the bomb with either solid carbon dioxide or liquid air.

The part of the apparatus enclosed in the dotted lines in Fig. IV was immersed in an oil thermostat insulated with about an inch and a half of powdered asbestos between the inner metal container for the oil, and the outer metal container. The top of the thermostat was covered with heavily shellaced beaver board with openings which could be covered to get at the stopcocks and other parts requiring attention. The stirrer consisted of two propellors on a shaft running along the axis of a three and a quarter inch steel tube which ran from about an inch below the upper oil surface to about an inch from the bottom of the thermostat. The electrical heating coil was placed in the upper part of this tube. A steel cylinder filled with mercury served for a thermal regulator in the customary manner.

VIII. CALIBRATION AND RESULTS WITH THE FIRST APPARATUS

The essential constants of the apparatus which are required are the volume of the bomb, the volume calibration curve of the injector, and the change of these with temperature, the guage constant for the piston pressure guage, and the thermometer calibration.

The volume of the bomb was obtained by the expansion of dry nitrogen from a container of known volume into the bomb. Pressures were measured by a mercury manometer by which pressures could be determined to two tenths of a millimeter of mercury or better. The known volume was a heavy glass bulb of slightly greater volume than the bomb. The volume of this bulb was determined by filling with air-free distilled water. Corrections were made in the calculations for the deviations from the ideal gas law of nitrogen by the Beattie-Bridgeman equation of state. The volume thus calculated for the bomb was 1106.7 cc. excluding the volume of the leads at 20°C. The volume of the gas leads to the stopcocks and the riser block including the gas space in the riser block was 2.9 cc. Thus the effective gas volume of the bomb at 20°C was 1109.6 cc. with a probable error figured from three determinations of the volume of ± .6 cc.

The injector was calibrated by filling with mercury under vacuum followed by weighing the amount of mercury ejected for various settings of the screw. Three such calibrations checked well to the ten thousandth of a cubic centimeter or 0.0001 cc. A calibration curve was drawn from which amounts of water injected for any definite number of turns of the injector could be calculated. This calibration was carried out at 27°C.

Since the highest temperature to be used was 90°C the coefficient of expansion of the bomb and injector was not required with great accuracy. It was considered sufficient therefore to take values from the literature. The mean value of the linear coefficient of expansion of brass between 20°C and 100°C was taken as 18.9×10^{-6} per degree C. from the data on various brasses from the International Critical Tables with the resulting cubical coefficient for the bomb of 56.7×10^{-6} per degree C. The linear coefficient of turbine steel was taken from the data of Hidnert and Sweeney.[23] for the same temperature range as 10.05×10^{-6}, and in consequence a value of 30.2×10^{-6} was taken for the cubical expansion of turbine steel.

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[23] Hidnert and Sweeney, Bur. Stand. Sci. Pap. 22, 639, (1928).

The piston pressure guage was calibrated by the vapor pressure of carbon dioxide liquid at the ice point according to the method of Bridgeman.[24] The constant thus determined was 0.99868 millimeters of mercury per gram weight on the pan at 30°C. The weights used with the guage were calibrated against standard weights.

Temperatures were measured by a platinum resistance thermometer of the calorimeter type, and calculated by the familiar Callendar formula. The thermometer was calibrated at the ice point, the steam point, and the sulphur boiling point, and the ice point was checked and corrected for at numerous times during the course of the work.

Water for injecting into the bomb was conductivity water which was boiled under vacuum before being introduced in the injector in order to get rid of dissolved gases as much as possible. The carbon dioxide used was commercial tank carbon dioxide which was passed over phosphorous pentoxide in a drying train to remove water. The remaining impurities were primarily traces of permanent gases in such quantities as to make further purification unnecessary for

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[24] Bridgeman, J. Am. Chem. Soc. 49, 1174, (1927).

work. A few runs were tried with better purification of the carbon dioxide by redistillation, but no difference could be detected in the results.

Some early measurements taken shortly after the apparatus was first assembled showed that by far the larger amount of the water injected could not be staying in the vapor phase, but was being adsorbed by the walls of the bomb. Although the bomb had been carefully washed out after soldering it was thought possible that flux still remained in the threads of the caps which had been soldered on. The bomb was consequently removed and steam passed in, allowing it to condense on the walls of the bomb. Chlorides were found present in the water which dripped from the bomb so the process was continued until the emerging water showed absolutely no test for chlorides.

It was found necessary after this treatment of the bomb to introduce very slight drops of vacuum pump oil on the bearings of the stirrer shaft in order to make the stirrer function properly. This was probably due to some oxidation of the brass bearing surface on steaming. On reassembly the apparatus was found to behave more nearly as it was expected to, and series of runs were made to test its characteristics more fully.

The most reproducible results were found to be obtained if the bomb was left between runs with water in the gas phase corresponding to between about a tenth and a third of the saturation quantity. Immediately before a run this was for the most part washed out by introducing carbon dioxide and then drawing it off until the pressure was down to about twice the value of the vapor pressure of water at that temperature. The bomb could then be refilled and the process repeated until only a negligible amount of water remained in the vapor phase. Evacuation below the vapor pressure of water was impossible due to the presence of liquid water in the capillary which would evaporate if the pressure were too low. The nature of the effects when this procedure was not followed indicated that there is probably some rather tightly held adsorbed water which is partically removed when the bomb is allowed to stand with no water vapor present. It is immediately readsorbed when water is injected. If the bomb is left near saturation between runs the adsorbed water will gradually come off the walls after the water vapor has been removed. Either of these effects would show up on the first few measured points of a run as was indeed the case.

It was furthermore found advisable never to inject water in sufficient quantities so that the drop of water formed fell off the capillary. If a drop fell evaporation would take place so slowly that it was almost impossible to tell when equilibrium was attained. Under normal conditions it was found that when the pressure had remained constant for between five and ten minutes equilibrium had been attained. The amount of water injected in any given run could not practically be carried beyond an amount about three quarters of that necessary to saturate the gas, as above that value equilibrium was too slowly attained to make measurements practical.

Series of runs were made at 50°C, 70°C, and 90°C. The initial pressures of carbon dioxide,calculated by estimating the amount of water injected previous to the first pressure reading,varied from 2.7 atmospheres to about 15 atmospheres measured with the piston pressure guage. A few runs at lower pressures were made at 50° and 70° by substituting for the piston guage a manometer with oil above the mercury in one arm of the manometer leading to the oil in the riser block. By varying the amount of mercury in the other arm of the monometer until the riser block balanced the pressure could be read.

In Tables V, VI and VII are given the data obtained at 50°. 70°and 90° respectively. It was found by calculation that the compression of the water in the injector system during any run due to the increase of pressure in the bomb was

TABLE V

50°C

Density H_2O liquid = .98807 g. per cc.
Compressibility = 47 x 10^{-6} per atm.
M = Millimols water injected per liter of volume
p = pressure in mm. of mercury

Run I		Run 2		Run 3	
M	p	M	p	M	p
.062	2237.3	.062	2238.8	.124	2241.8
.743	2250.2	.434	2245.5	.495	2248.8
1.610	2267.2	.805	2252.8	.867	2256.4
2.477	2282.4	1.672	2268.1	1.734	2272.1
3.344	2298.5	2.663	2286.7	2.725	2290.3
3.839	2307.1	3.406	2300.6	3.467	2304.1
4.227	2315.2	3.778	2307.4	3.839	2310.9
		4.149	2313.8	4.210	2317.3

Run 4		Run 5		Run 6	
M	p	M	p	M	p
.062	2026.0	.062	2540.7	.062	4293.7
.434	2032.7	.434	2547.5	.496	4300.8
.806	2039.6	.805	2554.2	.867	4307.8
1.673	2056.3	1.673	2570.5	1.735	4323.6
2.665	2074.5	2.664	2589.2	2.726	4341.6
3.421	2088.5	3.408	2602.6	3.470	4354.5
3.780	2095.0	3.780	2609.3	3.730	4359.0
4.152	2102.0	4.152	2615.9		

TABLE V continued

50°C

Run 7		Run 8		Run 9	
M	P	M	P	M	P
.062	3311.5	.062	6430.3	.124	5106.5
.334	3316.4	.372	6435.7	.434	-5111.9
.830	3325.5	.867	6444.7	.929	5120.8
1.573	3339.4	1.859	6462.4	1.921	5138.6
2.565	3357.9	2.850	6480.4	2.912	5156.2
3.321	3371.4	3.470	6490.8	3.655	5169.4
3.804	3377.9	3.594	6493.2	3.779	5171.5

Run 10		Run 11		Run 12	
M	P	M	P	M	P
.062	780.0				
.248	783.4	.136	452.6	.124	2325.6
.991	797.6	.310	455.8	.372	2330.6
1.982	816.4	1.053	469.7	.868	2340.2
3.034	836.3	2.168	491.0	1.611	2353.5
3.591	846.7	3.159	509.5	2.603	2372.2
				3.471	2387.8
				4.091	2399.0
				4.215	2401.2

TABLE V continued

50°C

Run 13		Run 14		Run 15	
M	P	M	P	M	P
.124	11,137.3	.248	9041.6	.186	8985.2
.372	11,141.7	.496	9045.6	.434	8989.2
.868	11,150.1	.991	9054.6	.929	8997.8
1.860	11,166.6	1.984	9071.2	1.920	9014.6
2.851	11,182.0	2.851	9086.3	2.912	9031.7
3.842	11,197.8			3.902	9048.1
4.215	11,204.1			4.398	9056.9
4.338	11,206.0				

Run 16		Run 17	
M	P	M	P
.124	11,165.2	.187	7829.3
.371	11,169.6	.495	7834.3
.868	11,177.4	.991	7842.8
1.983	11,195.5	2.106	7862.1
2.974	11,211.6	3.097	7878.6
3.842	11,226.0		
4.090	11,229.9		

TABLE VI

70°C.

Density H_2O liquid = .97781 g. per cc.
Compressibility = 48 x 10^{-6} per atm.

M = Millimols water injected per liter of volume.
p = pressure in mm. of mercury

Run 1		Run 2		Run 3	
M	P	M	P	M	P
.123	9961.3	.123	8048.4	.123	11,213.4
.736	9972.4	.736	8060.6	.735	11,223.7
1.963	9994.9	1.962	8084.0	1.961	11,246.9
4.416	10041.0	3.800	8119.3	4.414	11,291.1
6.869	10085.9	6.866	8177.4	6.866	11,336.4
8.709	10120.0	8.704	8212.0	8.705	11,369.7
9.322	10131.9	9.317	8223.8	9.317	11,380.9

Run 4		Run 5		Run 6	
M	P	M	P	M	P
.123	751.0	.061	763.6	.061	2235.4
.736	763.7	.612	775.1	.612	2246.3
1.962	789.4	1.838	800.5	1.838	2271.5
3.800	827.9	3.676	839.0	3.675	2309.3
5.638	866.1	5.514	877.5	5.514	2347.1
7.476	904.4	7.352	915.7	7.352	2384.7
9.130	938.8	8.578	940.8	8.577	2409.4

TABLE VI continued

70°C

Run 7 M	Run 7 P	Run 8 M	Run 8 P
.245	5094.2	.245	4377.2
.858	5107.2	.858	4389.3
2.083	5130.7	2.083	4413.9
3.921	5167.1	3.921	4450.9
6.372	5215.3	5.758	4487.4
7.597	5239.5	7.596	4523.9

TABLE VII

90°C

Density H_2O liquid = .96534 g. per cc.
Compressibility = 49 x 10^{-6} per atm.
M = Millimols water injected per liter of volume.
p = pressure in mm. of mercury

Run 1		Run 2		Run 3	
M	P	M	P	M	P
.242	2247.6	.242	2253.6	.242	4346.9
.847	2260.7	.846	2266.8	.847	4360.2
2.661	2300.6	2.660	2306.7	2.660	4399.3
5.081	2353.7	6.288	2386.3	6.288	4476.8
7.500	2406.9	9.915	2465.9	9.916	4554.4
9.918	2460.0	13.541	2544.8	13.544	4632.1
12.337	2513.0	17.168	2623.3	17.171	4709.0
14.765	2565.2	18.377	2649.2	18.380	4735.0
17.174	2617.6				
18.383	2643.5				

TABLE VII continued

90°C

Run 4		Run 5		Run 6	
M	P	M	P	M	P
.242	2078.9	.242	2322.5	.242	7845.1
.847	2093.4	.847	2335.8	.847	7858.4
2.662	2132.0	2.660	2375.7	2.663	7894.9
6.291	2212.1	6.288	2455.2	6.294	7969.8
9.920	2292.2	9.914	2534.6	9.925	8044.6
12.548	2371.2	13.541	2613.4	13.554	8118.4
17.176	2450.3	17.168	2691.8	17.183	8192.1
18.384	2476.2	18.378	2718.0	18.393	8217.0

Run 7		Run 8	
M	P	M	P
.242	10,234.1	.242	4641.9
.847	10,243.8	.847	4655.7
2.661	10,280.4	2.660	4694.3
6.291	10,353.5	6.288	4771.8
9.920	10,425.6	9.915	4848.9
13.549	10,498.0	13.543	4926.6
17.177	10,570.3	17.168	5002.8
18.387	10,594.6	18.376	5029.1

sufficiently small so that the error introduced in calculating the amount of water injected from the volume injected and the density at an average pressure during the run, figured from the density and compressibility of water, was negligible. The millimols of water injected per liter of gas volume was therefore 1000 times the volume injected, times the density at the average pressure, divided by the molecular weight of water 18.015 multiplied by the volume of the bomb in liters. The pressures given are corrected for the temperature of the pressure guage and variations in the barometric pressure.

The temperature for any run was within a hundredth of a degree of the temperature entered at the head of the table, and during each run the temperature measured by a platinum thermometer placed next to the bomb varied only three or four thousandths from the mean for that run.

It was found possible to fit each run to within the experimental error by an equation of the form

$$p - p_0 = C\,M + D\,M^2 \qquad (37)$$

where M is the millimols of water injected per liter and p the pressure. p_0 is the pressure of carbon dioxide in the bomb before any water was injected, and C and D are constants. The constant C was found to vary with the concentration of carbon dioxide, while D remained constant within the experimental error at any given temperature.

The initial pressure of carbon dioxide p_0 was figured from this equation by making an estimate of the amount of water present when the first pressure reading was taken, from the amount of water probably remaining after the washing out process with CO_2 before the run, and the amount injected before the first reading was taken. Since this quantity is small and D of equation (37) is also small the error in making the estimate has no appreciable effect on the solution for C and the error of a millimeter or so possibly introduced on p_0 will have no appreciable effect.

From these p_0 values the initial density of carbon dioxide in mols per liter was figured from the Beattie-Bridgeman equation of state for CO_2[15] in its complete form.

A best value of D was chosen at each temperature and, using this value, values of C were calculated for each run to fit the experimental data as well as possible. These quantities p_0, density CO_2, C and D are tabulated in Tables VIII, IX and X.

When p_0 becomes zero in equation (37), in other words, when the density of carbon dioxide is zero, then that equation should reduce to the equation of state for pure water which would be

$$p = R T M + R T \beta_0 M^2 \qquad (38)$$

TABLE VIII

Pressures and **Densities** of Carbon Dioxide, and Values of C and D for Runs at 50°C

RT = 20.152 liter mm. per millimol

D = -.020

Run No.	p_o	Density CO_2	C	C/RT
1.	2.938	.1121	18.66	.926
2.	2.939	.1121	18.52	.919
3.	2.942	.1123	18.62	.924
4.	2.660	.1014	18.66	.926
5.	3.335	.1275	18.50	.918
6.	5.635	.2174	17.90	.888
7.	4.347	.1668	18.32	.909
8.	8.440	.3294	17.76	.881
9.	6.701	.2596	17.80	.883
10.	1.023	.0389	19.02	.944
11.	.596	.0225	19.08	.947
12.	3.052	.1165	18.52	.919
13.	14.616	.5858	16.28	.808
14.	11.862	.4699	17.21	.854
15.	11.790	.4668	17.06	.847
16.	14.652	.5876	16.30	.809
17.	10.273	.4041	17.12	.850

TABLE IX

Pressures and Densities of Carbon Dioxide and Values of C and D for Runs at 70°C

RT = 21.400 liter mm. per millimol.

D = -.0170

Run No.	p_o	Density CO_2	C	C/RT
1.	13.072	.4849	18.62	.870
2.	10.563	.3884	19.08	.892
3.	14.715	.5490	18.32	.856
4.	.985	.0351	20.98	.980
5.	1.003	.0357	20.98	.980
6.	2.934	.1052	20.58	.962
7.	6.681	.2425	19.82	.926
8.	5.740	.2077	20.05	.937

TABLE X

Pressures and Densities of Carbon Dioxide and Values of C and D for Runs at 90°C

RT = 22.647 liter mm. per millimol

D = -.0150

Run No.	P_0	Density CO_2	C	C/RT
1.	2.945	.0996	22.060	.9740
2.	2.953	.0999	22.055	.9738
3.	5.700	.1944	21.595	.9536
4.	2.724	.0921	22.125	.9770
5.	3.043	.1030	22.030	.9728
6.	10.291	.3549	20.725	.9152
7.	13.436	.4675	20.210	.8924
8.	6.087	.2076	21.535	.9510

From the equation of state for mixtures equation (18) and equation (20) we should expect equation (37) to be more explicitly

$$p - p_0 = RT\left[1 + 2\beta_{012}\frac{n_{CO_2}}{V}\right]M + RT\beta_{01}M^2 \qquad (39)$$

Due to the fact that higher terms in the density have been omitted in this treatment it might be expected that deviations from this equation might result at high pressures, but we should expect that in our experiments C/RT plotted against the density of carbon dioxide N_{CO_2}/V would extrapolate smoothly to unity as n_{CO_2}/V approached zero. Such plots of the data are shown in Figures V, VI, and VII for the three temperatures in question. It can be seen that the results are linear within the probable experimental accuracy which increases with the temperature on account of the greater pressure range. However the extrapolations all come in to less than unity by amounts greater than can be accounted for by the scattering of the points.

This effect is undoubtedly due to adsorption on the walls of the bomb. Some of the water injected into the bomb is not staying in the vapor phase after evaporation, but is condensing out as an adsorbed phase on the walls. The effect is apparently primarily on the term C for D is about the order of magnitude we would be led to expect from preliminary equations of state for steam suggested by Prof. Keyes.

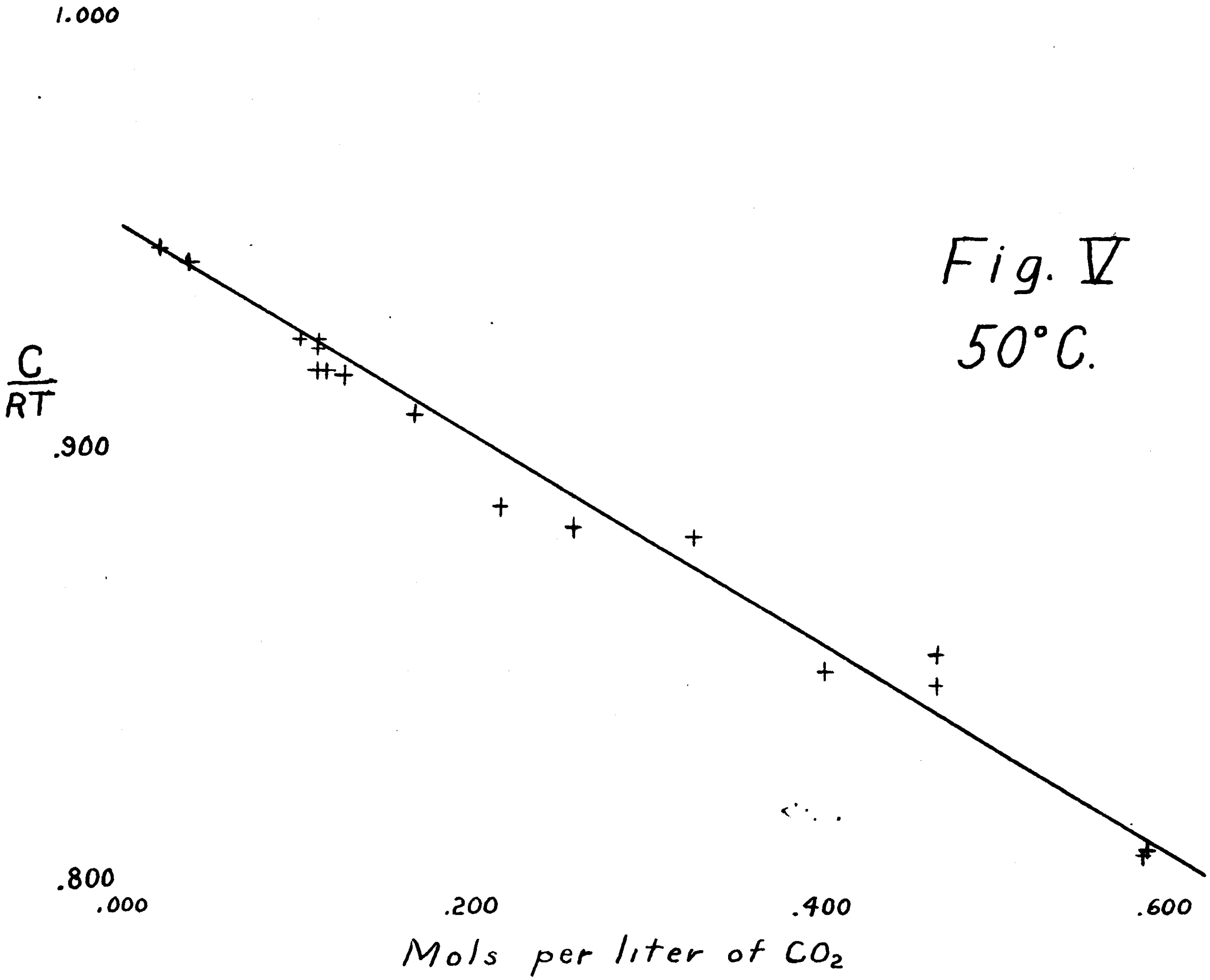

Fig. V
50°C.
1.000
C/RT
.900
.800
.000
.200
.400
.600
Mols per liter of CO₂

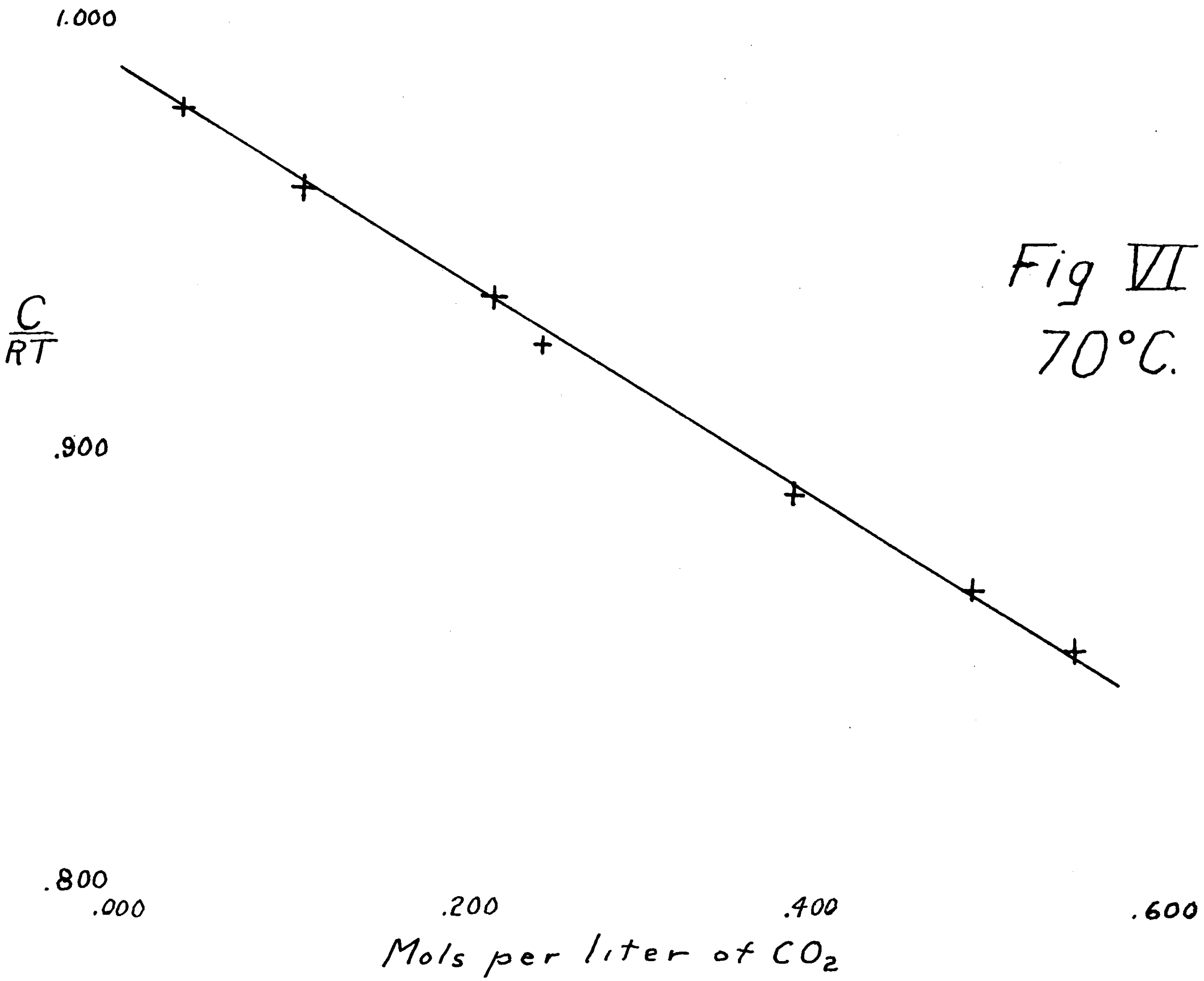

Fig VI
70°C.

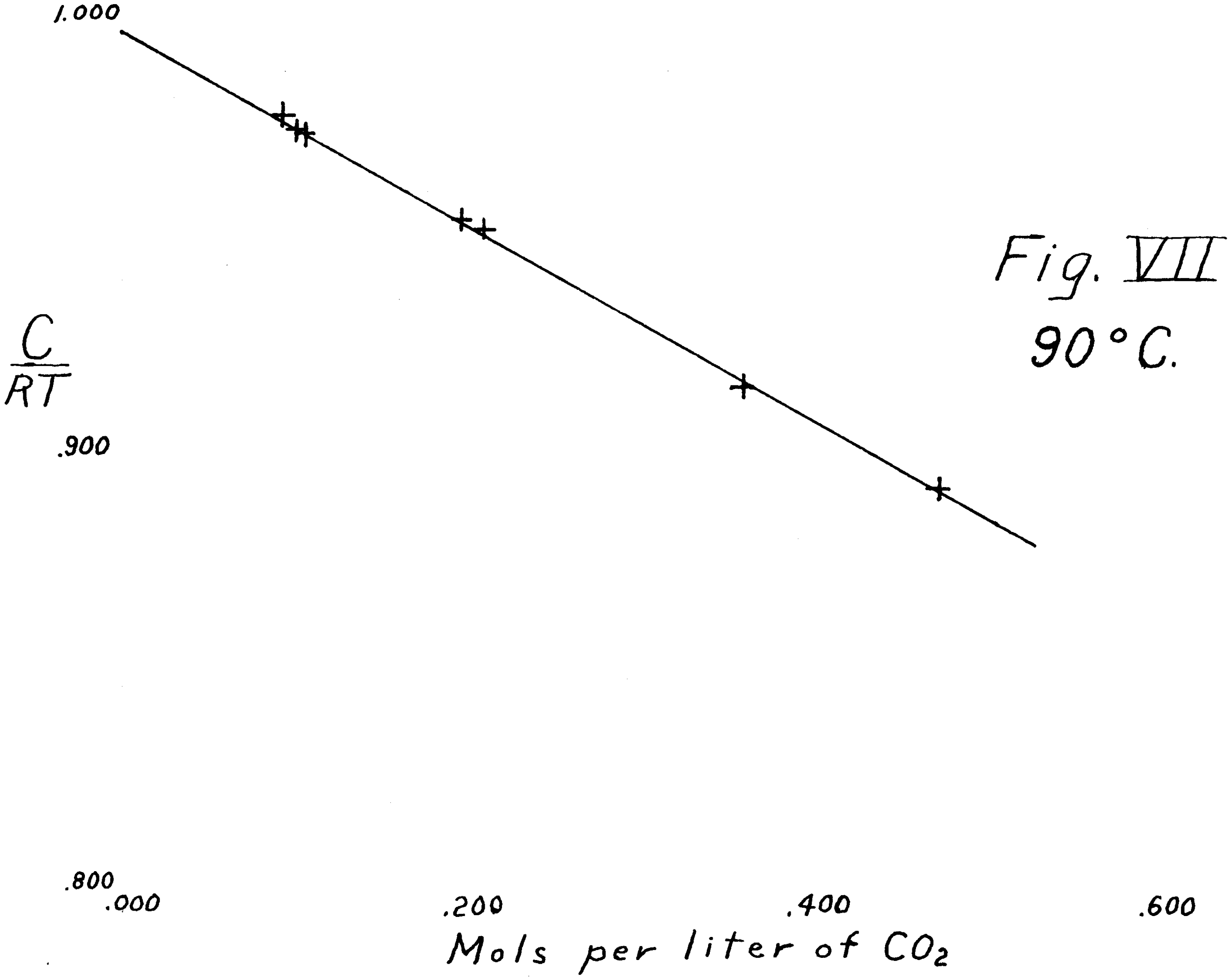

Fig. VII
90° C.

Although the amount of the adsorption correction is determined at zero concentration of carbon dioxide by the deviation of the intercept from unity, the variation of this correction with pressure is not known and cannot be predicted from theoretical considerations. The variation of the term C in equation (37) due to adsorption cannot of course be predicted in this way without a knowledge of the value of for steam.

An attempt was made to determine the amount of these corrections by introducing additional brass surface. For this purpose fine mesh brass screening was used. This screen had sixty wires per inch in one direction, and eighty wires per inch in the other. The calculated area of the bomb and exposed parts, such as the stirrer, was 105 square inches, and sufficient screen to make additional brass surface of 95 square inches was introduced. The surface of the screen was calculated from the length and number of the wires and their diameter. This screen was introduced in three spiral rolls after a steaming treatment similar to that given the bomb, and runs were carried out as before at 70° and a pressure of about three atmospheres.

The results of these runs were not too reproducible but gave results for which the D values for equation (37) were several times aslarge as those in the runs without the surface.

The only possible way of interpreting these results is that the surface added did not duplicate the original surface in adsorptive properties. It is thought possible that the many fine wires in intimate contact may have introduced capillary effects with consequent adsorption of a different character.

Since the inner surface of the bomb was practically black from corrosion, primarily from the steaming process necessary to remove flux from soldering it was decided to coat the inside of the bomb with some more resistant substance and to repeat the experiments. It was also decided to make other improvements in the details of the apparatus.

IX. MODIFICATIONS AND RESULTS WITH SECOND APPARATUS

In order to make the surface of the bomb less subject to corrosion it was at first attempted to silver plate it. It was found, however, practically impossible to obtain a coating of silver which would not blister when the reassembled bomb was soldered. It was consequently decided to tin the inner surface of the bomb. The inner surface of the bomb is coated with pure tin- and polished as much as possible. The stirrer mechanism and supports are silver plated since it is unneccessary to heat these sufficiently to blister, and the plating is more practical for these parts.

On the stirrer supports nine hooks are provided from which spirals of thin sheet tin and thin silver plated copper can be hund. These are to hang in such a position that the gas driven by the stirrer can blow through them freely, and the spirals of sheet metal eliminate almost entirely the metal to metal contacts which it is thought may have caused difficulties in the previous series of runs to determine adsorption. These spirals can readily be introduced through a half inch hole in the bottom of the bomb where the capillary is inserted.

On account of the considerable corrosion of the lead washers for the windows, and water injecting system it was decided to replace them with gold where ever they came in contact with either the gas or liquid water.

After carefully measuring the surfaces of the various parts, the bomb was reassembled and steamed out as before until no further traces of chloride could be detected. The volume of the bomb was calibrated as before and found to be 1105.5 cc. which gives a total gas volume for the apparatus of 1108.4 ± .6 cc at 25°.

The riser block contact became difficult to locate due apparently to some emulsification of mercury in the oil above which necessitated cleaning and refilling with mercury. In order to prevent this happening again the riser block contact current has been made an extremely small direct current which is amplified by a 201-A tube, which in turn operates a sensitive relay by which the making or breaking of the mercury contact causes a light to go off or on.

A new thermal regulator giving more consistent regulation was constructed in which the mercury is in an annular ring around the stirrer. This was deemed advisable due to the difficulty of satisfactory regulation with the old method, and the fact that irregularities in temperature control can have considerable effect on the small differences in pressure measured.

Near the end of the series of measurements about to be reported, the water injector broke in such a manner as to require a new piston, and screw. The reconstructed injector was calibrated as before, and used to complete the 90°C series. Except for the change and the change in volume of the bomb, the constants of the apparatus are the same as in the previous measurements. The inner surface of the bomb now consists of 92 square inches of tinned surface, 13 square inches of silver plated surface, and one square inch of glass surface.

Using the same experimental procedure as before, series of runs were made at 50°, 70° and 90°C. as before, and the results are reported in Tables XI, XII and XIII respectively. The same method of calculating and treating the data is used, and the values of the constants for equation (37) obtained for the runs along with the p_o values, and densities of carbon dioxide in mols per liter are presented in Tables XIV, XV and XVI. In Figures VIII, IX and X values of C/RT are plotted against the density of carbon dioxide $^{N}co2/_{V}$.

TABLE XI

50°C

Density H_2O liquid = .98807 g. per cc.
Compressibility = 47×10^{-6} per atmosphere.
M = Millimols water injected per liter of volume.
p = pressure in mm. of mercury

Run 1		Run 2		Run 3	
M	P	M	P	M	P
.062	2038.1	.062	2480.5	.062	6125.5
.310	2042.6	.248	2484.1	.310	6130.0
.683	2049.8	.621	2491.0	.683	6137.0
1.303	2061.7	1.241	2503.1	1.303	6148.0
1.924	2073.7	1.986	2517.2	1.924	6159.2
2.669	2087.8	2.607	2529.0	2.669	6172.4
2.917	2092.3	2.855	2533.6	2.917	6176.7

Run 4		Run 5		Run 6	
M	P	M	P	M	P
.062	6499.6	.062	7627.0	.062	4885.2
.310	6504.1	.310	7631.3	.310	4889.8
.683	6510.7	.683	7637.5	.683	4896.3
1.303	6521.5	1.303	7648.1	1.303	4907.8
2.048	6534.7	2.048	7661.4	1.923	4919.4
2.668	6545.6	2.668	7672.1	2.668	4932.8
2.917	6550.0	2.917	7676.3	2.916	4937.2

Table XI continued

50°C

Run 7		**Run 8**		**Run 9**	
M	P	M	P	M	P
.062	2270.9	.062	9178.2	.062	11,682.3
.310	2275.5	.372	9183.7	.434	11,688.7
.682	2282.9	.745	9190.1	.807	11,694.5
1.303	2294.7	1.490	9202.7	1.552	11,706.6
2.047	2308.7	2.234	9215.6	2.296	11,719.0
2.667	2320.7	2.855	9225.9	2.917	11.728.6
2.915	2325.4	3.103	9230.1	3.165	11,732.7

Run 10

M	P
.062	11,488.9
.434	11,494.8
.807	11,500.6
1.552	11,512.6
2.296	11,524.6
2.917	11,534.3
3.165	11,538.6

TABLE XII

70°C

Density H_2O Liquid = .97781 g per cc.

Compressibility = 48×10^{-6} per atm.

M = Millimols water injected per liter of volume.

p = pressure in mm. of mercury.

Run 1		Run 2		Run 3	
M	P	M	P	M	P
.123	6328.8	.123	8723.4	.123	11,561.1
.737	6340.9	.737	8734.8	.737	11,572.2
1.964	6364.7	1.964	8758.2	1.965	11,594.7
3.806	6400.8	3.806	8792.7	3.806	11,628.4
6.261	6448.3	6.262	8839.3	6.262	11,672.8
7.489	6472.1	7.490	8862.1	7.490	11,694.8
8.103	6483.6	8.104	8873.8	8.104	11,705.8
		8.717	8885.1	8.718	11,716.7

TABLE XII continued

70°C

Run 4		Run 5		Run 6	
M	P	M	P	M	P
.123	2052.2	.123	2048.4	.123	5031.4
.736	2064.9	.737	2061.2	.737	5043.6
1.963	2090.2	1.964	2086.4	1.964	5068.1
3.803	2128.1	3.806	2124.4	3.806	5104.8
6.256	2178.5	6.262	2174.9	6.261	5153.4
7.483	2203.4	7.489	2199.9	7.489	5177.5
8.096	2214.9	8.103	2212.3	8.103	5189.6

Run 7	
M	P
.123	12,153.0
.737	12,154.1
1.351	12,165.2
2.579	12,187.2
4.421	12,220.0
6.877	12,264.0
8.105	12,285.8
8.719	12,296.5

TABLE XIII

90°C

Density H_2O liquid = .96534 g per cc.

Compressibility = 49 x 10^{-6} per atm.

M = Millimols water injected per liter of volume.

p = pressure in mm. of mercury.

Run 1		Run 2		Run 3	
M	P	M	P	M	P
.242	12,773.5	.242	2571.9	.242	5947.7
1.455	12,797.0	1.452	2598.6	1.454	5973.2
3.879	12,844.1	3.874	2651.6	3.876	6024.6
7.514	12,915.0	7.505	2731.1	7.509	6101.2
11.149	12,985.1	11.137	2810.2	11.142	6177.7
14.784	13,055.5	14.769	2888.8	14.774	6253.5
17.207	13,102.1	17.191	2940.9	17.196	6303.8
18.419	13,125.3	18.401	2966.8	18.407	6328.7

TABLE XIII continued

90°C

Run 4		Run 5		Run 6	
M	P	M	P	M	P
.242	10,410.6	.242	12,237.8	.356	5165.8
1.454	10,435.3	1.454	12,261.9	1.544	5191.1
3.876	10,484.1	3.877	12,310.6	3.921	5241.9
7.510	10,557.4	7.512	12,382.1	7.487	5318.0
11.144	10,630.0	11.146	12,453.7	11.053	5393.7
14.777	10,702.4	14.780	12,524.2	14.615	5468.3
17.199	10,750.2	17.202	12,571.2	16.989	5518.3
18.410	10,773.3	18.414	12,594.6	18.177	5542.8
				19.366	

Run 7		Run 8	
M	P	M	P
.356	2,050.7	.356	9459.7
1.542	2,077.1	1.545	9484.0
3.913	2,129.4	3.922	9532.3
7.469	2,207.7	7.487	9604.9
11.024	2,285.5	11.050	9676.9
14.579	2,363.0	14.612	9748.2
16.950	2,414.3	16,987	9795.4
18.137	2,439.5	18.175	9819.1
19.324	2,465.0	19.364	9842.6

TABLE XIV

Pressures and Densities of CO_2, and constants for Runs at 50°

RT = 20.152 liter mm. per millimol

D = -.020

Run No.	p_o	Density CO_2	C	C/RT
1.	2.680	.1022	19.19	.950
2.	3.263	.1247	19.09	.945
3.	8.059	.3140	17.99	.890
4.	8.551	.3339	17.65	.874
5.	10.034	.3943	17.39	.861
6.	6.426	.2487	18.35	.908
7.	2.986	.1140	19.19	.950
8.	12.075	.4787	17.05	.844
9.	15.371	.6184	16.15	.799
10.	15.115	.6074	16.09	.796

TABLE XV

Pressures and Densities of CO_2, and constants for Runs at 70°

RT = 21.400 liter mm. per millimol

D = -.0170

Run No.	p_o	Density CO_2	C	C/RT
1.	8.324	.3038	19.58	.9125
2.	11.475	.4233	18.98	.8845
3.	15.209	.5684	18.27	.8510
4.	2.697	.0966	20.69	.9640
5.	2.692	.0964	20.70	.9645
6.	6.617	.2401	19.97	.9305
7.	15.988	.5992	18.03	.8400

TABLE XVI

Pressures and Densities of CO_2, and Constants for Runs at 90°

RT = 22.647 liter mm. per millimol

D = -.0180

Run No.	p_o	Density CO_2	C	C/RT
1.	16.801	.5900	19.715	.8687
2.	3.377	.1143	22.090	.9732
3.	7.819	.2679	21.340	.9402
4.	13.691	.4766	20.340	.8962
5.	16.096	.5642	19.960	.8795
6.	6.787	.2319	21.510	.9476
7.	2.688	.0919	22.210	.9785
8.	12.437	.4315	20.505	.9035

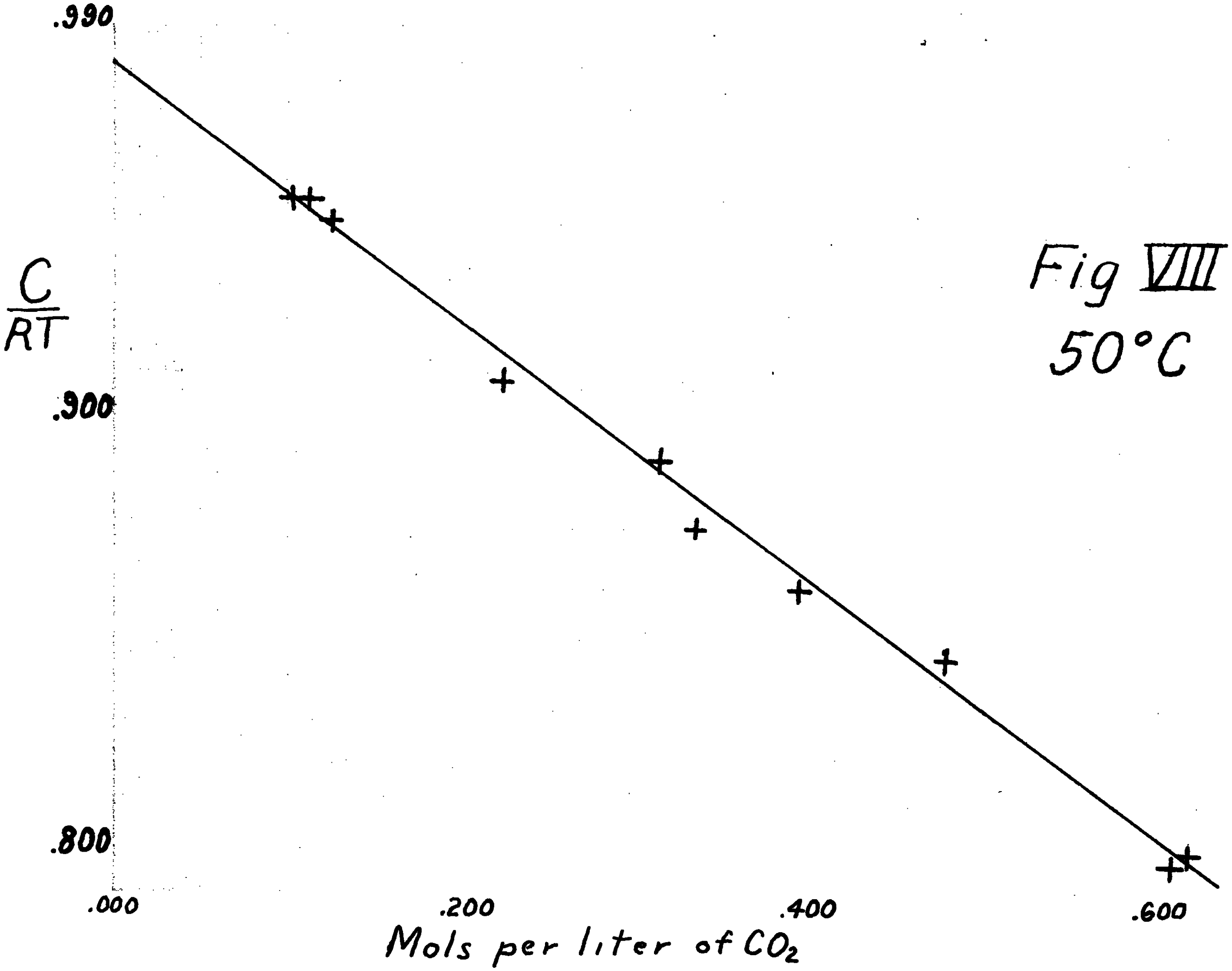

Fig VIII
50°C

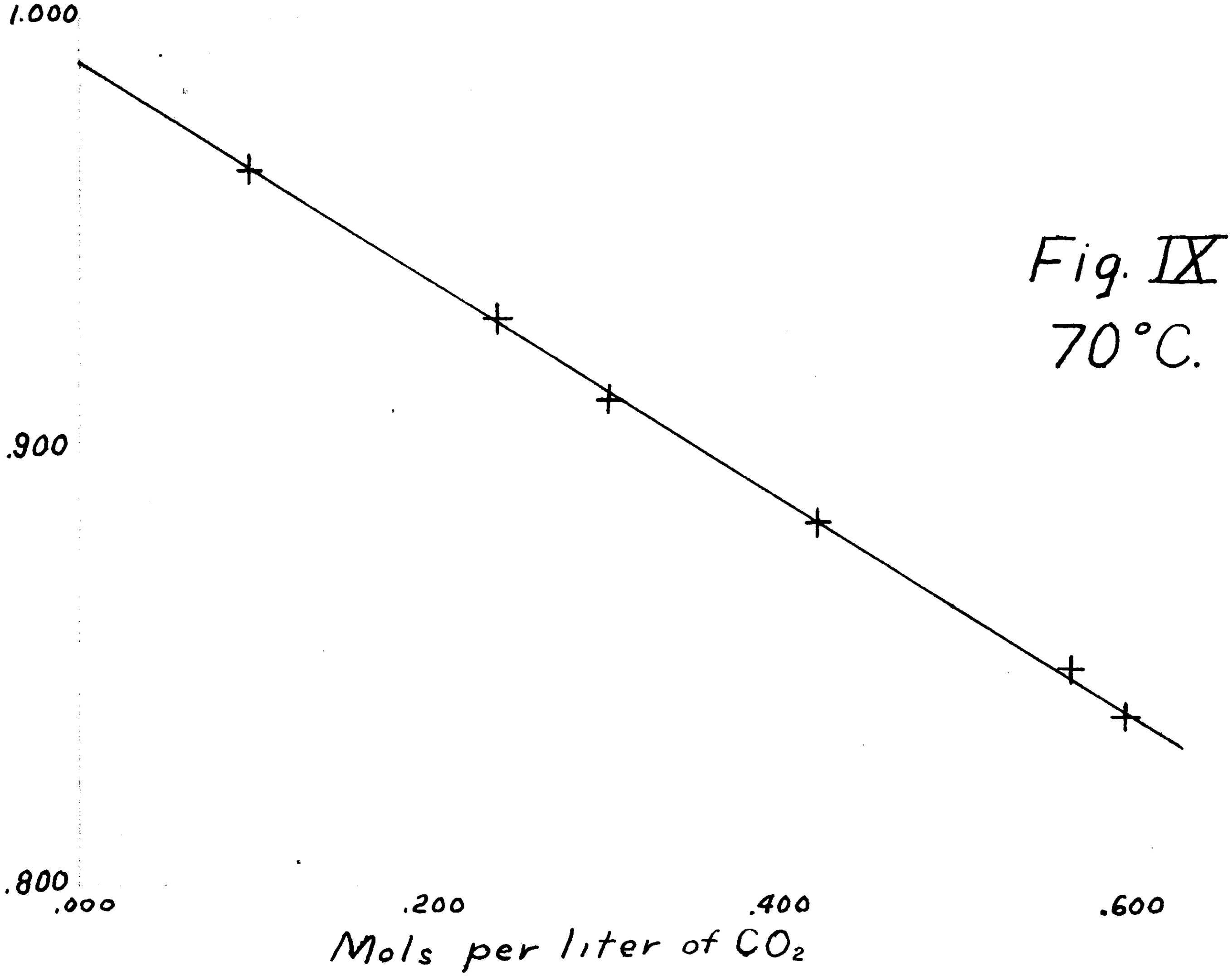

Fig. IX
70°C.

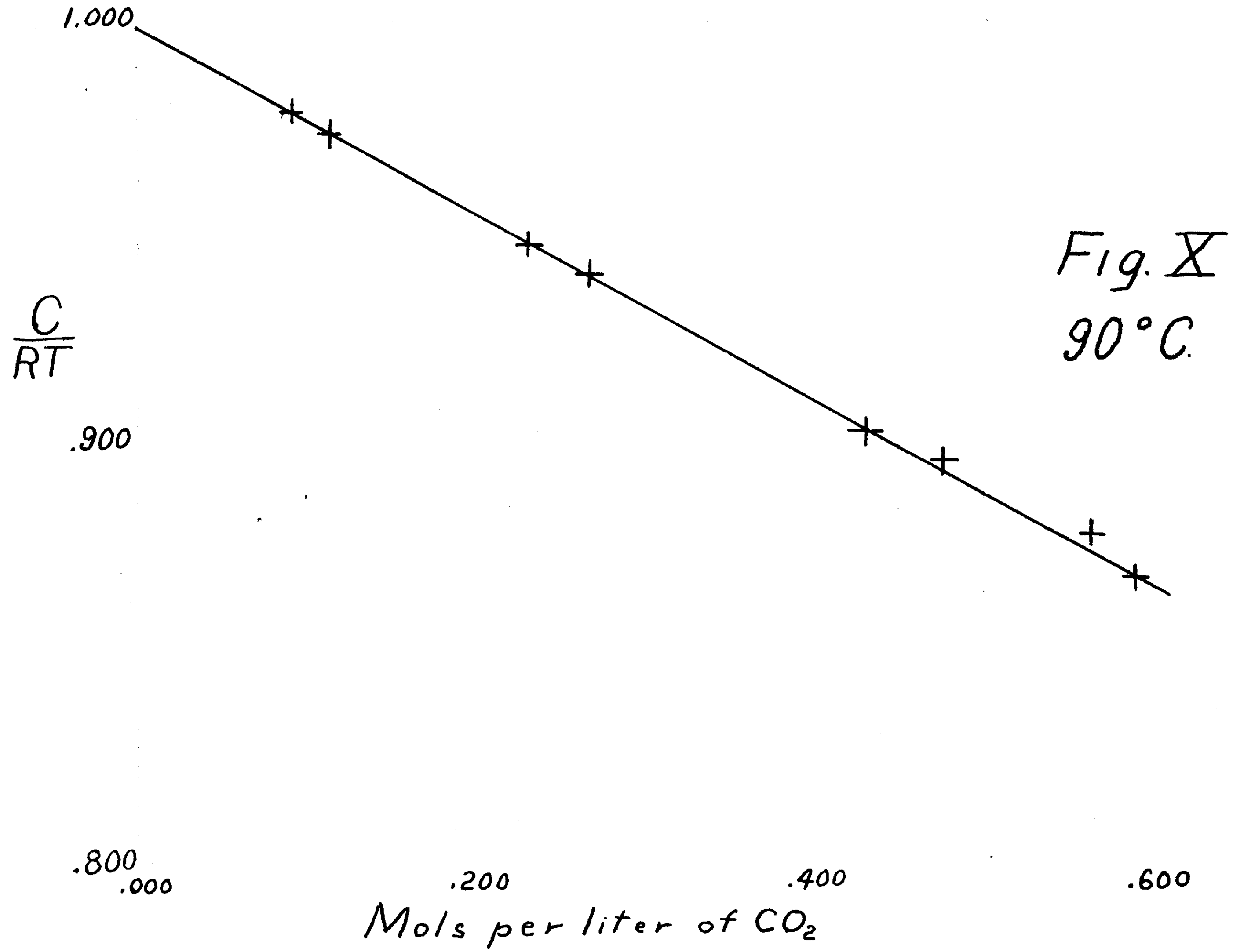

Fig. X
90°C.

It will be noted that in this case also the straight lines on the plots of C/RT which represent satisfactorily the experimental data do not extrapolate at zero concentration of carbon dioxide to unity. Except for the 50°C isotherms the intercepts are almost identical with those of the previous series. This divergence in the case of the two 50°C series is probably to be explained on the basis of errors in the first series. This series was the first made, and the technique of obtaining reproducible results had not been fully learned. At 50°C the experimental total difference in pressure between the initial reading, and the final reading in any run is only a matter of about sixty millimeters, so that small systematic errors can produce large percentage effects in the results. Due to the minor modifications in the apparatus, and the refinements in technique the second series is to be considered far more trustworthy, particularly at 50°.

In order to make a comparison of the two series more readily we shall express the results of each isotherm in an equation of the form of equation (39).

$$p - p_o = RT\left(A + B\,\frac{n_{co2}}{V}\right)M + DM^2 \qquad (40)$$

where A B and D are constants for each isotherm. The values of these constants are tabulated in Table XVII. The dimensions of A are those of a pure number, those of B, liters per mol, and those of D millimeter liters squared per millimol squared.

Table XVII

Empirical Constants for Experimental Isotherms

Series	Temp. °C	A	B	D
I	50°	.952	-.240	-.020
I	70°	.989	-.246	-.017
I	90°	.996	-.224	-.0150
II	50°	.981	-.298	-.020
II	70°	.989	-.248	-.017
II	90°	.998	-.222	-.0180

It can be noted that in spite of the marked changes in the surface of the bomb that the results are in quite close agreement, except for the two 50° isotherms previously mentioned. The constant D, which is not determined with any great precision due to its small effect in the experiments can be taken the same in both series at the two lower temperatures with no decrease in the accuracy of representation of the data. At 90° the values of D are taken somewhat different for the two series in order to get the best representation of the experimental data. The small difference in D is probably due in part to the adsorptive properties of the surfaces. Even at this temperature where D is more important than at the lower temperatures it is probably not uniquely determined to better than five percent by the experiments.

The bomb is so arranged that added surface to duplicate as nearly as possible that already present may be conveniently added. Such experiments should give to a fairly good precision the adsorption correction onthe constants listed in Table XVII. The correction on A must of course be such as to bring A to unity in all cases.

In the meantime, it is possible on the basis of the present experiments to make a provisional calculation of the fugacity of water in mixtures with carbon dioxide by assuming that the adsorption of water at a given temperature is dependent only on the concentration of water in the bomb and that adsorption has a negligible effect on the term D. This will be carried out for the two upper temperatures 70° and 90° and should particularly in the case of the 90° isotherms yield a result of fairly good precision, due to the smallness of the adsorption correction.

The result of these assumptions is that A is placed equal to unity in equation (40), and the other constants remain the same. This means graphically that the true curves of Figures IX and X are taken to be ones parallel to the given curve, but passing through unity for zero concentration of carbon dioxide. Average values of B and D for the two series are used. Equation (40) with these constants, combined with equations (9) and (11), give for the fugacity at 90°C.

$$\log f_1 = \log \frac{M}{33.559} - .0968 \frac{n_2}{V} - .00063 M \qquad (41)$$

while at 70°C

$$\log f_1 = \log \frac{M}{35.515} - .1073 \frac{n_2}{V} - .00069 M \qquad (42)$$

where f_1 is the fugacity of water in atmospheres, log denotes common logarithms, n_2/V is the density of carbon dioxide in mols per liter, and M as before the millimols of water per liter.

While the results at 70° may be subject to a greater error than those at 90° due to a lack of a true adsorption correction, it is worth while to compare these results with a few measurements by Pollitzer and Strebel[8] on the concentration of water vapor in carbon dioxide saturated with water at 70° and higher pressures than we have used. By the use of the fugacities given by equation (42) and the assumption that the solubility of carbon dioxide in water is linear from one stmosphere to the pressures used, for the calculation of a Raoult's law correction, we calculate the results given in Table XVIII.

TABLE XVIII

Observed Percentage Differences in Concentration of Water Vapor in Carbon Dioxide at 70°C from those calculated.

Total Pressure in Atmospheres	% Excess Water Observed over Gibbs-Dalton law	% Excess Water Observed over Values given by Equation (42)
29.5	33.8	0.8
37.7	49.1	2.6
50.3	78.9	6.2
50.5	80.7	7.1

These deviations are all on the same side and might be accounted for by the small correction to equation (42) necessary on account of adsorption. The accuracy of the solubility correction of carbon dioxide in water is doubtful by enough to cause a possible error of one or two percent at these pressures, and the accuracy of the measurements was probably not above one percent. Taking into account, therefore, the severe extrapolation of our results to high pressures, the check of equation (42), which is only intended for use up to about 16 atmospheres, is very satisfactory.

The question of the difficulties introduced by adsorption, which has been from the start one of the vital problems of this type of measurement, seems to present no insurmountable difficulties. The fact that there is adsorption does not prevent obtaining reproducible results even with such different surfaces as we have used in our two series of measurements. Moreover, at higher temperatures results of reasonable accuracy can be obtained by making very simple assumptions concerning adsorption, as the comparison with the data of Pollitzer and Strebel shows. It is expected that by the introduction of added surface, provision for which has been made, adsorption corrections can be made with considerable accuracy even at lower temperatures. It seems probable, therefore, that the experimental method for measuring the isothermal variations of the chemical potential, and the apparatus for that method which we have devised will be quite satisfactory for its purpose.

X SUMMARY

A general discussion of the methods of measuring the variations of the chemical potential of gas mixtures with density and composition are given. Two new methods not heretofore used are proposed for taking data on the pressure, volume, temperature, composition relations of gas mixtures in such a way that the calculation of the variation of the chemical potential is facilitated.

The equation of state treatment for calculating chemical potentials by means of the method of combination of constants is applied to the existing data on iodine in mixtures with carbon dioxide, hydrogen, and air in such a way as to devise equation of state constants for iodine. These constants make possible the calculation of the chemical potentials in the mixtures given above, and are applied to derive better values of the vapor pressure of iodine.

One of the experimental methods proposed for the taking of equation of state data in order to facilitate calculating the variations of the chemical potentials has been tried experimentally on mixtures of carbon dioxide and water. Certain difficulties are encountered on account of adsorption of water on the walls of the bomb, but even neglecting these difficulties values of the chemical potential at 70°C can be obtained which are in good agreement with the existent data. Provisions have been made for evaluating the adsorption effect experimentally. The results obtained show that the apparatus constructed is suitable for measuring the isothermal variations of the chemical potential.

BIOGRAPHICAL DATA

Harold Tirrell Gerry was born in Hartford, Connecticut in February, 1908. His elementary and secondary school education was primarily in the Cambridge, Mass. public schools. He entered the Massachusetts Institute of Technology in 1925 from the Cambridge High and Latin School. The degree of Bachelor of Science in Chemistry was awarded him by M. I. T. in 1929. In that year he entered the Research Laboratory of Physical Chemistry as a graduate student, and during the year of 1931-1932 was a Research Assistant in that laboratory. Two articles have been published from that laboratory in collaboration with Professor Gillespie; "Densities and Partial Molal Volumes of Ammonia, for the Ammines of Calcium and Barium Chlorides", (Gillespie and Gerry, J. Am. Chem. Soc. 53, 3962, (1931)) and "The Calculation of Normal Vapor Pressures from the Data of the Gas Current Method, Particularly in the Case of Iodine", (Gerry and Gillespie, Phys. Rev. 40, 269, (1932)).