that some of the new lines may correspond to so-called forbidden lines will greatly interest those who like to look in that way at lines that are not explained by the electron theory.

THE PRESSURE VARIATION OF THE HEAT FUNCTION AS A DIRECT MEASURE OF THE VAN DER WAALS FORCES

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The heat function or thermodynamic potential, \( \chi = \varepsilon + p v \), where \( \varepsilon \) is the energy, \( p \) the pressure and \( v \) the volume, is a function of the greatest importance in the applications of thermodynamics to chemistry and engineering. In the present note a brief account will be given of a direct method whereby it has been found possible to determine the change of \( \chi \) with pressure at constant temperature.

The differential coefficient \( \left( \frac{\partial \chi}{\partial p} \right)_T \) possesses among other properties a most intimate relation to the departure of gases from the simple equation \( p v = R T \). It will be shown that the coefficient is most closely related to and is, in fact, a measure of, the molecular van der Waals forces, attractive and repulsive, operative in giving to gases their known physical properties.

Starting with Gibbs' equation \( (90)^1 \) we find

\[
\left( \frac{\partial \chi}{\partial p} \right)_T = T \left( \frac{\partial S}{\partial p} \right)_T + v + \sum_{\mu} \left( \frac{\partial m_{\mu}}{\partial p} \right)_T
\]

(1)

where \( S, \mu \) and \( m \) represent the entropy, the thermodynamic potential and the mass. The change of entropy with pressure under the conditions of constant temperatures is equivalent to \( - \left( \frac{\partial v}{\partial T} \right)_p \) assuming the state of the system to be only a function of the variables \( P \) and \( T \). In the special case of a single pure substance (1) becomes,

\[
\left( \frac{\partial \chi}{\partial p} \right)_T = v - T \left( \frac{\partial v}{\partial T} \right)_p = \left( \frac{\partial v}{\partial \tau} \right)_p \]

(2)

where \( \tau \) is used to denote \( T^{-1} \).

The Joule-Thomson coefficient, \( \left( \frac{dT}{dp} \right) = \eta \), is given on the other hand
by the formula

$$\eta = -\frac{\left(\frac{\partial \chi}{\partial \rho}\right)_T}{\left(\frac{\partial \chi}{\partial T}\right)_\rho} = -\frac{\left(\frac{\partial \chi}{\partial \rho}\right)_T}{C_p}. \quad (3)$$

It is evident therefore that an experimental method capable of giving precise values of $\left(\frac{\partial \chi}{\partial \rho}\right)_T$ will lead to values of the heat capacity where Joule-Thomson data are available. It is to be noted also that an empirical knowledge of the $p-v-T$ properties is obtainable, for setting $\left(\frac{\partial \chi}{\partial \rho}\right)_T$ equal to $C$ we find from integrating (2)

$$\left[(v\tau)_1 - (v\tau)_2 = \int_{n}^{\tau} C d\tau\right]_p. \quad (4)$$

Thus if the value of $v\tau$ be known, say along the vapor saturation curve, values of $v$ at higher temperatures are deducible for constant pressure from a knowledge of the $C$'s. If the method of obtaining the latter is simple and moderately exact, very exact values of the volumes of the fluid can be deduced. If at the same time $\eta$ values are available, a very convenient method of obtaining the heat capacity, $C_p$, over a range of temperature and pressure becomes possible.

For an ideal gas $\left(\frac{\partial \chi}{\partial \rho}\right)_t$ is zero. However, for an ideal gas mixture having convertible components the coefficient would have a finite value. Thus considering the simple case of the reaction $2A \leftrightarrow A_2$ where $\alpha$ is used to represent the fraction of the $A$ molecules converted to $A_2$, we obtain for $\alpha \rightarrow 0$,

$$\left(\frac{\partial \chi}{\partial \rho}\right)_t = \frac{R\alpha}{2\rho} \left[\left(\frac{\partial f(T)}{\partial \tau}\right)_\rho - T\right] \quad (5)$$

where $\frac{\partial f(T)}{\partial \tau}$ is proportional to the heat,

$$-(\Delta U^o + \Sigma \nu_i \int C_{\nu_i} dT)$$

required to convert $2A$ to $A_2$. An experimental value of $\left(\frac{\partial \chi}{\partial \rho}\right)_T$ would therefore determine $\alpha$ provided the heat of the reaction were known or should $\alpha$ be known values for the heat of the reaction may be derived.

Actual gases having convertible components are, of course, far from ideal but the method here proposed promises, at least in those cases where
the reaction velocity is large, to be a convenient and accurate means of determining the properties of such mixtures. Further and more detailed discussion of this subject will be resumed in a later communication.

The procedure used in the present investigation, \[ \left( \frac{\partial x}{\partial p} \right)_T \text{positive} \], consists in allowing the gas to escape under a measured pressure through a platinum capillary tube into a region of lower pressure while generating heat in the capillary electrically to maintain the system at constant temperature. The electrical energy is expended in the wall of the capillary itself and if the bore and cross sectional area of the wall are uniform the expansion of the gas is isothermal.

The apparatus is represented in the figure. The calorimeter shell \( H \) and thermometer tubes \( T_1 \) and \( T_2 \) are made of pyrex glass. To facilitate assembly and adjustment of the parts, the shell is made in two pieces which can be united by means of the ground joint. \( B \) is a thin-walled copper tube 12 meters in length and 5 mm. in diameter, the greater part of which has been flattened and wound into a coil \( C \). This coil serves to bring the temperature of the incoming gas substantially to that of the bath which surrounds the apparatus. From the copper coil the gas passes through the ground joint \( D \) (metal to glass) to the thermometer tube \( T_1 \) in which is suspended a platinum ribbon constituting a resistance thermometer. The thermometer is unsheathed so that the winding is in actual contact with the gas stream. \( T_1 \) communicates with \( T_2 \) through the platinum capillary tube \( A \) which is one meter long, 0.5 mm. in bore and 0.1 mm. wall thickness.

Expansion of the gas occurs in the capillary. In case there is a tendency to cool (the method as here described is applicable only to those cases in which there is a fall in temperature), electrical energy is brought in through current leads made of No. 24 copper wire and contained in the cables \( e_1, e_2 \). A second thermometer
(similar to that in \( T_1 \)) in \( T_2 \) indicates the temperature of the outgoing gas. The fall of pressure across the capillary is measured by a mercury manometer, the two arms of which are connected to the heads of the thermometer tubes.

From \( T_2 \) the gas is led through a suitable absorption train where it is collected for measured intervals of time and weighed. The amount of heat supplied to the capillary is computed from potentiometer measurements of the voltage drops across the capillary and across a standard resistance in the same circuit.

Under ordinary operating conditions the temperature of the capillary has been found to be about one-third degree higher than that of the bath. Because of the temperature gradient a small fraction of the heat escapes to the bath. The space surrounding the capillary is highly exhausted so that heat may only be lost by radiation to the walls and by conduction from the ends of the capillary. The loss of heat is quite small but must be taken into account.

The pure platinum capillary is used as a resistance thermometer, the resistance being computed from the current and potential drop measurements made during the experiment. The current leads \( e_1, e_2 \) are double and during the measurements the heating current is borne by the two leads in parallel. For the blank run a current approximately half as large and supplied by a separate battery is caused to flow along one of the current leads and back through its double without entering the capillary. The same is done with the double leads at the other end of the capillary. These currents will produce about the same heating effect in the leads as the original current during the experiment. A third current is now superposed upon the others and directed through the capillary to bring its temperature to the desired magnitude. Its energy value is the correction that has been applied to the experimental results.

Two gases have been used thus far: \( \text{CO}_2 \) and \( \text{NH}_3 \). The observed values of \( \left( \frac{\partial x}{\partial p} \right)_T \) as well as those calculated by means of an equation of state for the gases\(^2\) are tabulated below:

<table>
<thead>
<tr>
<th>( T ) (C)</th>
<th>( p ) (MEAN)</th>
<th>Observed</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 )</td>
<td>300.23</td>
<td>2.459</td>
<td>8.889</td>
</tr>
<tr>
<td>( \text{NH}_3 )</td>
<td>300.23</td>
<td>1.890</td>
<td>58.542</td>
</tr>
<tr>
<td></td>
<td>300.23</td>
<td>1.511</td>
<td>58.212</td>
</tr>
</tbody>
</table>

The experimental values are in excellent agreement with the values computed by means of the equation of state based on \( p-v-T \) data at higher pressures. Unless the observed quantities are affected by unrecognized
errors they appear to be reliable to about 1 in 200 which at the low pressures of the measurements corresponds to very precise \( p-v-T \) data. Thus in the case of \( \text{NH}_3 \) at 1.9 atm. consistent \( p-v-T \) data to about 1 in 7000 would be required to enable \( \frac{\partial x}{\partial p} \) to be computed to within 1 part in 200.

The method in fact appears to be especially adapted to low pressure and low temperature experimentation; a particularly desirable feature since the technique of making \( p-v-T \) measurements is complicated, time consuming and at low temperatures difficult. The low temperature region is of course quite important from the point of view of extending the existing knowledge of the van der Waals forces.

The relation of the quantity \( \frac{\partial x}{\partial p} \) or \( \frac{\partial \varphi_T}{\partial T} \) to the intramolecular or van der Waals forces may be exhibited by using the equation of state in the form,

\[
\varphi = \frac{RT}{v - B}
\]

\[
B = 2\pi N \int (1 - e^{-\epsilon/kT}) r^2 dr.
\]  

(6)

The classical expression\(^3\) for \( B \) is valid for low pressures but not too low temperatures\(^4\) where quantized collision states become of sufficient importance to require consideration.

The expression for \( \frac{\partial \varphi_T}{\partial T} \) using (6) becomes \( \frac{\partial B_T}{\partial T} \), a function of \( T \) alone. If \( B \) is computed for the classical van der Waals' molecular model there is obtained:

\[
\frac{\partial B_T}{\partial T} = \beta - \frac{2A}{RT} - 3a_1 \frac{A^2}{RT\beta} - \frac{1}{\beta}
\]

or

\[
B = \beta - \frac{A}{RT} \left( 1 + a_1 \frac{A}{RT\beta} + a_2 \frac{A}{RT\beta} \right)
\]  

(7)

where \( \beta \) is the four-fold volume of the molecules, \( A \) corresponds to the \( a \) of van der Waals' special form of equation and \( a_1, a_2, \ldots \) are constants calculable when the law of attractive force is known.

It is clear from the foregoing that the present method of determining \( \frac{\partial x}{\partial p} \) may be regarded as a direct experimental procedure for obtaining exact information regarding molecular forces in gases. It is evidently particularly convenient for investigations at low temperatures; a region where values of the effects of the van der Waals forces and data for gaseous heat capacities\(^5\) is of great importance in guiding theoretical developments.

Equation 6 can be formulated for the case of a mixture of non-convertible
or non-reacting gas mixtures, thus enabling values of \( \left( \frac{\partial x}{\partial p} \right)_T \) for such mixtures to be used to guide the equation of state theory for mixtures. This is of interest, for a complete knowledge of the van der Waals forces in mixtures is of profound importance in the application of thermodynamics to chemical equilibria at finite pressures.

6 An innovation in the technique of measuring the Joule-Thomson effect to be reported later has been developed which is adapted to low temperatures and low pressures. From the two effects \( \left( \frac{\partial T}{\partial p} \right)_x \) and \( \left( \frac{\partial x}{\partial p} \right)_T \), the value of \( c_p \) is immediately deducible. (Eq. 3.)

PROOF OF GIBBS' HYPOTHESIS ON THE TENDENCY TOWARD STATISTICAL EQUILIBRIUM

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In this paper the author applies the circle of ideas due to B. O. Koopman1 and J. v. Neumann2 to the proof of Gibbs' fundamental hypothesis concerning the tendency of an ensemble of independent systems toward statistical equilibrium.3 The motions of the systems are described by a Hamiltonian differential system,

\[
q_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}.
\]

The ensemble is represented by a certain distribution in phase \( f(P)dm \), where \( P = (p_i, q_i) \), and where \( dm = \pi dq_i dp_i \) is the invariant volume element in the phase space. The distribution is carried by the phase flow associated with \( (H) \) and will, in general, alter in time. Under what conditions has \( (H) \) the property that any initial distribution tend toward a permanent one (not affected by the motions, i.e., being invariant under the flow)? Simple examples show that this tendency does not always exist.3 After giving an appropriate mathematical formulation of the tendency toward permanent distributions the author derives various necessary and sufficient conditions that a given flow show that tendency.