

configurations, (A) $5s^25p^65d^66s^2$, or (B) $5s^25p^66s^2-6p^6$. It is a significant and generally accepted fact that the negative oxidation states of all other elements involve the formation of stable s^2p^6 octets, and on this basis one is inclined to assign configuration B to Re^{-1} . This configuration, which requires the promotion of all of the original $5d$ electrons to the $6p$ orbital, would be in accord with the marked instability and strong reducing character of Re^{-1} .

Summary

A zinc reductor is described in which reduction can be performed conveniently at a controlled temperature and in the absence of oxygen. The fact that -1 rhenium is produced when ice-cold and air-free solutions of perrhenate ion in dilute sulfuric and perchloric acids are reduced with zinc has been confirmed by oxidimetric titration of the reduced solutions.

Polarograms of solutions of -1 rhenium in 1 to 2 *N* sulfuric acid at 0° display three anodic waves, whose half-wave potentials are (α) -0.54 v., (β) -0.34 v., and (γ) -0.07 v. *vs.* the saturated calomel electrode. A similar polarogram is obtained in 1 *N* perchloric acid with the following exceptions: (a) the β -wave is resolved into two separate waves, β' and β'' , whose half-wave potentials are -0.42 and -0.26 v., and (b) the half-

wave potential of the γ -wave is about 0.1 v. more positive than in sulfuric acid medium. Diffusion current data show that corresponding waves in the two media pertain to the same oxidation states and in both media the diffusion currents are directly proportional to the concentration of -1 rhenium. From the ratio of the heights of the various waves it is concluded that the α -wave results from the oxidation of -1 rhenium to the $+2$ state, the β' -wave to the $+3$ state, the β'' -wave to the $+5$ state and the γ -wave to complete oxidation to the $+7$ state (ReO_4^-). This conclusion has been confirmed by amperometric titration of the reduced solutions with ceric ion. Evidence is presented which indicates that the reversible potential of the reaction $\text{Re}^{+2} + 3e = \text{Re}^{-1}$ is equal to, or slightly more negative than, -0.54 v. *vs.* the saturated calomel electrode in dilute sulfuric or perchloric acid medium at 0° .

Partially oxidized solutions, obtained by warming dilute sulfuric acid solutions of -1 rhenium to about 50° for an hour in the absence of oxygen, show an *average* oxidation state of $+1$. However, the polarogram of such a solution indicates that the rhenium is not actually present in the $+1$ state, but as a mixture of Re^{-1} and higher states in proportions that are equivalent to an average oxidation state of $+1$.

CAMBRIDGE, MASSACHUSETTS RECEIVED JUNE 15, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

The Accommodation Coefficient of Mercury on Platinum and the Heat of Vaporization of Mercury

BY LLOYD B. THOMAS AND FRANCOIS G. OLMER

Introduction

We have been interested in applying the Pirani type pressure gage as a means of determining small total pressures of pure gases and as a means of following quantitatively the progress of gas reactions at low pressure. Such an application to mixtures in which some gaseous compounds are consumed and others produced requires an accurate knowledge of the free molecule heat conductivity of each gas from the surface of the specified filament material. This actual heat conductivity is conveniently expressed in terms of the calculated free molecule heat conductivity and the accommodation coefficient. Since there is available only an admittedly rough estimate of

the accommodation coefficient of mercury¹ on platinum and since, in this case, pressures are established in equilibrium with liquid mercury and the measurements apparently lead to a precise method of determining the heat of vaporization which should be generally applicable, we are submitting this work under separate title.

Experimental

A diagram of the tube used is shown in Fig. 1. The filament consists of 31.5 cm. of 0.004 inch c. p. platinum wire (Bishop Company) hung in a loop from tungsten leads in a Pyrex tube 3.0 cm. in diameter. At a distance of 4.5 cm. from the ends of the filament, potential leads of 0.001 inch c. p. platinum wire of 3.0 cm. length are welded on the

(1) W. B. Mann, *Proc. Roy. Soc. (London)*, **A146**, 786 (1934).

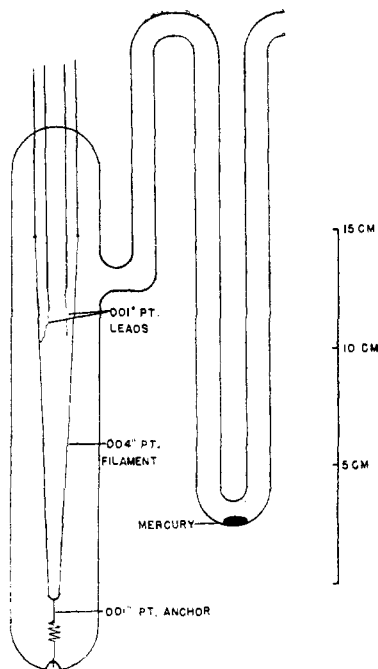


Fig. 1.—Tube I.

main filament and these are led out through two more tungsten seals. At the bottom of the loop a third 0.001 inch platinum wire was attached and this was anchored to the bottom of the tube. This latter was found necessary to eliminate vibration and to prevent the filament being pulled to the glass by electrostatic forces.

A diagram of the electrical circuits is shown in Fig. 2. The temperature coefficient of resistance of the filament was determined with the tube immersed in an oil-bath at temperatures from 0 to 150°. The resistance of the filament at any temperature is given by $R_t = R_0(1 + 0.0039055t)$ where R_0 is the resistance at 0°, t is the centigrade temperature of the filament, and 0.0039055 is the temperature coefficient. To operate the apparatus, the resistance between the potential leads at the desired filament temperature was calculated by the preceding equation and this value was set to the nearest 0.1 ohm on R_2 . Current in the filament was then adjusted by means of R_3 (two dial boxes in parallel) until the fall in potential over the filament and R_2 became equal. The current in the circuit and the temperature of the filament were then established accurately by measuring the potential drop across R_1 , a N. B. S. type 10 ohm standard resistor with potential contacts. Upon addition of gas the temperature of the filament was again adjusted to the original value by decreasing R_3 and the measurements for determining the new power loss were taken for the new condition.

The experimental tube was connected through a "U" tube and mercury cut-off to a high vacuum system employing the usual condensation pump, mercury cut-offs, McLeod gage, etc. No stopcocks were in the high vacuum line. The mercury vapor pressure was controlled by adjusting the temperature of a droplet of mercury in the "U" tube by means of a Dewar partially filled with water. When necessary this temperature was held constant and the bath stirred by passing air cooled in ice-water

into the Dewar at the proper rate to counter the heat leak. The tube itself was immersed in a thermostat containing kerosene held at 30°, about 5° above room temperature.

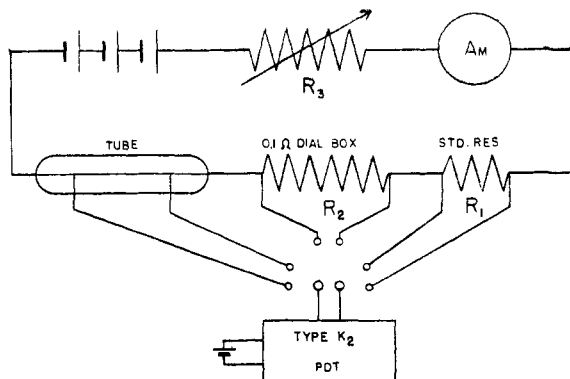


Fig. 2.—Electrical circuit of tube I.

Measurements and Treatment of Data.—

The power loss from the filament is measured for a series of mercury vapor pressures from 0 to 15×10^{-4} mm. The filament current is increased with each increase of mercury vapor pressure to bring the temperature of the filament to its original value in order to keep the radiation losses constant. The power losses are plotted against the vapor pressures of mercury at the various control bath temperatures according to the values given in the "International Critical Tables," Vol. III. These vapor pressures are corrected for the thermal transpiration pressure according to the formula $P_t = P_u \sqrt{T_t/T_u}$, in which P_t and P_u are the pressures of mercury in the experimental tube and in the "U" tube, respectively, and T_t and T_u are the corresponding absolute temperatures. To check the applicability of the above formula measurements were made using a 2-mm. capillary as the left arm of the "U" tube of Fig. 1, but no difference could be observed between these measurements and the ones using the uniform 9-mm. "U" tube shown in Fig. 1. The capillary was removed for the data reported here to facilitate thorough evacuation. The mean free path of the mercury atoms at the highest pressures used is at least three times the diameter of the tubes in which the temperature gradients occur, thus giving conditions under which the above transpiration formula holds.

A typical plot of power loss from the filament against corrected mercury vapor pressure (for a filament temperature of 224° in this case) is shown in Fig. 3. The points are seen to fall on a well defined straight line. To obtain such a line

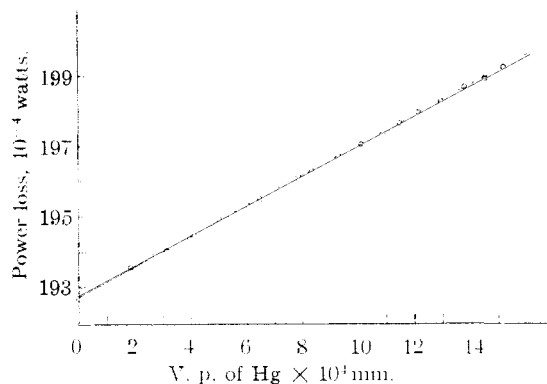


Fig. 3.

it was necessary to make measurements with the mercury cut-off which separates the system of Fig. 1 from the vacuum system closed. Runs made with the system open to the pumps showed a consistent behavior which we have been unable to explain. The observed behavior in such a case may be described with reference to Fig. 3. If the straight line is the best line which can be put through the points, the points lie regularly on an arc below the line from 0 to 6×10^{-4} mm., cross over at 6×10^{-4} and form an arc above the line from 6×10^{-4} to about 10×10^{-4} , and then cross back below the line and appear to lie on a third arc. The deviation of the arcs at the mid-points from the line is of the order of two to three times the radius of the circles of Fig. 3. Each of the four curves taken in this manner has the same form.

The slope of the curves as shown in Fig. 3 is the actual energy lost from the filament surface per second by gas conduction per unit of mercury vapor pressure. This, of course, may be reduced to the power lost per square centimeter of filament surface, per degree temperature difference between the wall and filament per bar of mercury pressure. This quantity will be designated by " $\Lambda_{\text{obs.}}$ " The theoretical heat conduction, designated as " $\Lambda_{\text{calcd.}}$ " from a square centimeter of surface per second per degree per bar, assuming complete temperature equilibrium of the rebounding molecules with the surface, has been calculated from kinetic theory to, varying degrees of refinement. We have used the expression²: $\Lambda_{\text{calcd.}} = \frac{1}{2}(\gamma + 1)C_v P' / (2\pi RT')^{1/2}$ in which γ is the ratio of specific heats, C_v the specific heat at constant volume, P' the pressure, T' the temperature of the gas concerned. In this case with mercury

(2) Kennard, "Kinetic Theory of Gases," McGraw-Hill Book Co., Inc., New York, N. Y., 1938.

T' is practically the same as the temperature of the wall since the mean path of mercury atoms is of the order of the radius of the tube at the highest pressures used, and the ratio of area of wall to area of filament is of the order of 150. We have used the values $\gamma = 1.67$, $C_v = \frac{3}{2}R$, $R = 8.316 \times 10^7 / 200.6$ ergs/deg. \times gram. The accommodation coefficient is the ratio of $\Lambda_{\text{obs.}} / \Lambda_{\text{calcd.}}$. The values which we have obtained for the accommodation coefficient of mercury are tabulated below. For completeness under the title of this paper and to throw evidence on a point discussed below we have included a set of accommodation coefficients measured with a tube, designated Tube II, in which filament lead losses have been eliminated.³

Tube I		Tube II	
ΔT	a	ΔT	a
36.6	0.967	36.3	0.969
114	.910	112	.905
194	.840	199	.844
		202	.828
		275	.757

These values of a are plotted against the corresponding values of ΔT in Fig. 4. The curve has two notable features, namely: the limiting accommodation coefficient as ΔT approaches zero is very close to unity assuming the extrapolation to be valid; and the accommodation coefficient falls off in approximately linear fashion as ΔT increases. This is the only case which we have seen of a simple molecule for which an accommodation coefficient of unity is reported. A high accommodation coefficient is generally associated with a long time of contact of the molecules with the surface or, *i. e.*, strong adsorption tendencies.

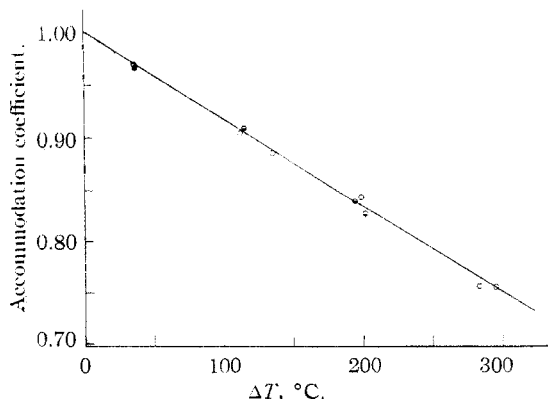


Fig. 4.—O, Values with tube II; ●, values with tube I.

(3) Description of Tube II to be published currently.

(4) ΔT is the temperature difference between the filament and wall, the latter being 30°.

Keesom and Schmidt⁵ have investigated the accommodation coefficients of several gases on glass and have drawn the conclusion that below the critical temperature the heat conduction in a rarified gas becomes independent of the surfaces and the accommodation coefficient becomes unity. From this point of view it is not surprising that the value for mercury is unity since its critical temperature is above 1500°. It is commonly assumed that the accommodation coefficient is independent of the temperature difference, ΔT , of the filament and the impinging gas molecules.⁶ This seems to be tacitly assumed at least in defining the accommodation coefficient in which no restriction is made that ΔT approach zero for the determination of its value. In view then of the fact that a value of unity is obtained for the coefficient as $\Delta T \rightarrow 0$ and that, according to Keesom and Schmidt's generalization, it should remain unity to high filament temperature, we are inclined to doubt that the accommodation coefficient is independent of the ΔT at which it is measured. It would be quite improbable that the wall temperature, 30°, chosen in this work happened to be the unique temperature at which the accommodation coefficient of mercury on platinum begins to digress from unity. We suspect that the fall in accommodation coefficient is due primarily to an increasing ΔT rather than an increasing filament temperature. The work of Mann¹ and Mann and Newell⁷ on platinum filaments points toward the possibility of another cause of the observed behavior. Their filament surfaces have been freed from contamination, presumably, by heating to high temperature and accommodation coefficient measurements have been taken as soon as possible after lowering the temperature. The initial values obtained in this way are much lower than those obtained before heating the wire, and the values rise with time and approach the original value. This behavior is attributed to the cleaning and subsequent contamination of the surface with adsorbed gas. The behavior observed in the present work could be due to the decreasing extent of adsorption at higher temperature of some gas present in the system—water vapor for example or mercury itself—and hence a changing surface upon which the accommodation coefficient is measured. However,

(5) Keesom and Schmidt, *Physica*, **3**, 590 and 1085 (1936); **4**, 828 (1937).

(6) See for example J. K. Roberts, *Proc. Roy. Soc. (London)*, **A129**, 146, 147 (1930).

(7) Mann and Newell, *ibid.*, **158**, 401 (1937).

all such effects, if present, must have been rapidly reversible as no inconsistencies or erratic behavior commonly associated with filament surfaces of varying degree of cleanness were evident. In our work the tube was frequently baked out thoroughly at 400°, the tubing of the vacuum system heated with a large brush flame, and the filament temperature raised to 800° during the course of the experiments.

Some points concerning the accuracy of the measurements should be considered. The diameter of the filament was checked by two methods—comparing the observed resistance at 0° and length of the filament with the resistivity of platinum (60.0 ohms per mil. foot), and comparing the mass of a portion of the filament material of known length with the density. Both methods agree with the specified diameter to well within one per cent. The filament shows some striation and general roughness under the microscope. No attempt was made to determine the extent of increase in area (above that calculated) due to roughness, but it should be mentioned in this connection that the accommodation coefficients of hydrogen and helium on the same filament material are 0.23 and 0.17, respectively, and the emissivity from this filament material is approximately 20% greater than that given for bright platinum in the "International Critical Tables" over the temperature range 300 to 700°K. The temperature of the filament as measured in this work is a mean value between the potential leads. The resistance of platinum has a very nearly linear dependence on temperature and the heat conducted to the wall by the gas has a similar dependence on the temperature of the filament. The temperature distribution over the portion of the filament between the potential leads is far from constant in vacuum, and this distribution will be modified with addition of gas giving rise to concealed changes in power loss not due to gas conduction itself but due to changes in the temperature gradients in the filament at the leads and in the potential leads themselves and due to changes in the radiation loss, which is proportional to the temperature to the fourth power, over the new temperature distribution. It is believed that the errors from this source are negligibly small in these measurements on mercury for the following reasons: first, the slope of the power loss *vs.* pressure curves is constant both with mercury and with permanent gases up to pressures corresponding to

many times the gas heat conduction attained in these experiments on mercury vapor; second, values of the accommodation coefficient obtained in a tube constructed to eliminate end losses, and hence having constant filament temperature over the entire length, agree with those obtained with this tube; third, the approximate calculations of the temperature distributions with and without gas show that the above suspected uncertainties would be very small for mercury. Concerning the accuracy of the electrical measurements it should be said that all voltages were read to the limit of the L. and N. Type K-2 potentiometer using a L. & N. galvanometer of 0.005 μ a. sensitivity and 33-ohm resistance. The 10-ohm resistor is guaranteed to a tolerance of 0.01%, and the standard cell was checked against cells recently certified by the Bureau of Standards. The resistance of the filament was adjusted for each measurement in a set to within 0.0005 ohm of the chosen value and the value of R_0 for the filament was checked from time to time. The power loss by gas conduction varied from 11% of the total with the filament at 66° to 3.3% with the filament at 225°.

Measurement of the Heat of Vaporization of Mercury at 10°.—A great many sets of values for the vapor pressure of mercury are in the literature. If we use sets of vapor pressure data differing from that of the "International Critical Tables," different slopes for the curves of the type plotted in Fig. 3, and hence different values for the accommodation coefficient will be obtained. The vapor pressure and accommodation coefficient are mutually indeterminate by the method of this paper, but the measurements allow a determination of the heat of vaporization of mercury which of course has its bearing on any set of vapor pressure data through the equation

$$\frac{d \ln p}{dT} = \frac{\Delta H_v}{RT^2}$$

By subtracting the power loss in vacuum, W_{vac} , from that at each temperature of the vapor pressure control bath, W_T , one obtains numbers which are proportional to the pressure of mercury vapor P_T in the experimental tube at the temperature of the thermostat bath, 30°. One has then $W_T - W_{vac} = \Delta W_T$. The assumption can then be made that $\Delta W_T = kP_T$ which is justified by the experimental fact that it is found to be true with permanent gases for which the pressure can be measured directly with the McLeod gage. To determine the heat of vaporization one is interested in

the pressure of mercury vapor in contact with the liquid mercury in the "U" tube and this is less than P_T by a thermal transpiration correction factor as mentioned earlier. Designating the equilibrium vapor pressure in the "U" tube by P_T (eq.) one may write

$$\begin{aligned} \Delta W_T \sqrt{\frac{T}{303}} &= kP_T \text{ (eq.)} \\ \ln \Delta W_T + \frac{1}{2} \ln (T/303) &= \ln k + \ln P_T \text{ (eq.)} \\ \ln \Delta W_T \text{ (cor.)} &= \ln k + \ln P_T \text{ (eq.)} \\ \frac{d \ln P_T \text{ (eq.)}}{dT} &= \frac{d \ln \Delta W_T \text{ (cor.)}}{dT} = \frac{\Delta H}{RT^2} \text{ or} \\ \frac{d \log_{10} \Delta W_T \text{ (cor.)}}{d 1/T} &= - \frac{\Delta H}{R \times 2.303} \end{aligned}$$

The values of $\log_{10} \Delta W_T$ (cor.) for five sets of data were plotted against $1/T$ and the slopes of these curves multiplied by $R \log_{10} e$ (4.575 cal./deg.) give $-\Delta H_{vap}$ for mercury. The points lie in regular fashion and seem to show a slight curvature in the proper direction to give smaller values of ΔH_{vap} at the higher temperatures. We have taken the slopes of the best lines we could put through the points over the temperature range 0–20°, and our results give the heat of vaporization at approximately 10°. The results of five runs from both Tube I and Tube II are tabulated below.

$T_{fil.}$, °C.	Tube	ΔH_{vap} .
66	I	14898
144	I	14897
224	I	14923
232	II	14951
315	II	14930

The mean deviation from the average is 0.12%. We have not made a critical study of the measurements of others on this ΔH_{vap} value, but we can say that our value, 14920 calories, is not outside the probable limits for the correct value.

This method seems to us to offer attractive possibilities as a means of determining heats of vaporization or sublimation of compounds over temperature ranges such that the vapor pressure varies from 10^{-5} up to 10^{-2} mm. If desired, the thermostat could be operated at any temperature and the filament can be operated from a few degrees above this up to as high as desired as long as it does not cause decomposition of the compounds investigated. We hope to test the method on some organic compounds of convenient volatility.

Summary

The accommodation coefficient of mercury on

platinum has been measured at low mercury pressures. It has been found to approach unity as the temperature difference between the filament and wall approaches zero and to fall off about 0.08 for each 100° of this temperature difference. The data obtained in the measurements allow a calcu-

lation of the heat of vaporization of mercury. It is suggested that the method might be developed into a precise and convenient one of wide applicability for determining heats of vaporization and sublimation.

COLUMBIA, MISSOURI

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[CONTRIBUTION FROM PHYSICAL CHEMISTRY LABORATORY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE SCHOOL OF APPLIED SCIENCE]

Equation of State for Gases at High Pressures Involving Only Critical Constants

BY SAMUEL H. MARON AND DAVID TURNBULL

Several years ago F. G. Keyes,¹ starting with an equation of state involving PV as a linear function of pressure, deduced generalized equations for polar and non-polar gases at low pressures. More recently the authors,² using the principle of corresponding states, presented a method for estimating the Beattie-Bridgeman constants of any gas from those of a reference gas. The only supplementary data required were the critical pressures and temperatures of a gas and of the reference, for which nitrogen was taken. The success thus attained suggested that the pressure range over which calculations could be made could be extended appreciably provided an equation of state were available covering a wider range of pressures than that of Beattie-Bridgeman. Consequently an empirical equation of state for nitrogen was deduced, covering the temperature range of -70 to 600°, and for pressures up to 1000 atmospheres.³ The purpose of this paper is to show how this equation for nitrogen may be extended to other gases, and to present evidence for the validity of such an extension.

Derivation of Equation of State

The nitrogen compressibility data within the temperature and pressure ranges specified are represented with good reproducibility by the equation,³

$$PV = RT + \alpha_1 P + \alpha_2 P^2 + \alpha_3 P^3 + \alpha_4 P^4 \quad (1)$$

where the virial coefficients $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ are functions of the temperature only, and are given by

$$\alpha_1' = a_1 + \frac{a_2}{T} + \frac{a_3}{T^2} \quad (2)$$

$$\alpha_2' = \frac{b_1}{T^2} + \frac{b_2}{T^4} + \frac{b_3}{T^6} \quad (3)$$

$$\alpha_3' = \frac{c_1}{T^2} + \frac{c_2}{T^4} + \frac{c_3}{T^6} \quad (4)$$

$$\alpha_4' = \frac{d_1}{T^2} + \frac{d_2}{T^4} + \frac{d_3}{T^6} \quad (5)$$

$a_1, a_2, \dots, b_1, b_2, \dots$, etc., are constants independent of temperature and pressure. From (1) the expression for the compressibility coefficient, Z , of nitrogen follows as

$$Z = \frac{PV}{RT} = 1 + \frac{\alpha_1 P}{RT} + \frac{\alpha_2 P^2}{RT} + \frac{\alpha_3 P^3}{RT} + \frac{\alpha_4 P^4}{RT} = 1 + \left[\frac{\alpha_1' P_c'}{RT_c'} \right] \frac{P_r}{T_r} + \left[\frac{\alpha_2' (P_c')^2}{RT_c'} \right] \frac{P_r^2}{T_r} + \left[\frac{\alpha_3' (P_c')^3}{RT_c'} \right] \frac{P_r^3}{T_r} + \left[\frac{\alpha_4' (P_c')^4}{RT_c'} \right] \frac{P_r^4}{T_r} \quad (6)$$

where the substitutions $T = T_c' T_r$ and $P = P_c' P_r$ have been made for T and P . T_c' and P_c' are the critical constants of nitrogen, while T_r and P_r are the reduced temperature and pressure corresponding to T and P .

Now, the indications of various attempts at generalized correlation of compressibilities of gases^{4,5} are that Z is, to a fairly close approximation, a function of T_r and P_r only. If this statement be accepted provisionally, then it must follow that at any given values of T_r and P_r Z is the same for different gases, and hence the quantities in brackets in equation (6) must have the same values for all gases obeying the principle of corresponding states. Applying this identity condition to the first quantity in brackets in (6), we obtain for the relation between the primed quantities for nitrogen and the unprimed quantities for any other gas

$$\frac{\alpha_1 P_c}{T_c} = \frac{\alpha_1' P_c'}{T_c'} \quad (7)$$

$$\alpha_1 = \left(\frac{\alpha_1' P_c'}{T_c'} \right) \frac{T_c}{P_c}$$

(1) Keyes, *THIS JOURNAL*, **60**, 1761 (1938).

(2) Maron and Turnbull, *Ind. Eng. Chem.*, **33**, 408 (1941).

(3) Maron and Turnbull, *THIS JOURNAL*, **64**, 44 (1942).

(4) Dodge, *Ind. Eng. Chem.*, **24**, 1353 (1932).

(5) Lewis, *ibid.*, **28**, 257 (1936).