THE SECOND VIRIAL COEFFICIENT FOR STEAM*

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Abstract—Adsorption of water on the walls of the container is invoked to explain the non-linear course of the isothermal experimental values of $v(pv/RT - 1)$ and $v \ln (pv/RT)$ as small steam densities are encountered. It is noted that the known magnitude of the adsorption of water vapor on glass is in accord with the low density behavior of the quantities $v(pv/RT - 1)$ and $v \ln (pv/RT)$ and indeed the quantitative relationships for the 440°C steam isotherm are satisfactory. For the determination of the second virial coefficient the superiority of the extrapolation function $v \ln (pv/RT)$ is exhibited. The advantages of $(\partial h/\partial p)$ measurements as a means of deducing virial coefficients free from adsorption disturbances are illustrated and comparisons are made with virial coefficients deduced from p,v,t, data.

THE second virial coefficient for a gas is an important quantity required for describing analytically the p,v,t, properties and certain derived properties (the enthalpy, entropy and specific heat) assuming that a knowledge of the "zero" pressure specific heat is available. The coefficients are defined through the well known relation,

$$pv = RT(+B_0/v + B_1/v^2 +$$ (1)

where B_0 and B_1, etc. are the virial coefficients.

The determination of the coefficients has often been based upon the use of the experimental values of pressure and volume along the isotherms. Thus by forming the isothermal quantities, $v[(pv/RT) - 1]$ and entering the values as ordinates in a rectangular diagram with densities as abscissae, the intersections of the projected curves with the ordinate axis gives in principle the values of the B_0 coefficients for zero density. The tangent at B_0 will be the value of B_1. The procedure is essentially simple and it would appear that, since the value of R, the gas constant, is accurately known exact and consistent pressure-volume data are only required to lead to reliable values of the coefficients.

It will be perceived that an inaccurate determination of B_0 entails an inaccuracy in B_1 and succeeding coefficients. Consequently any factors which affect the accuracy of the low pressure and the corresponding volume measurements are important. For illustration, at 100°C for steam the value of B_0 is known to be $-24\cdot5$ cm³/g and the saturation volume is close to 1673·5 at one atmosphere, but B_0 in this instance is only 1·465 per cent of 1673·5 and volumes and pressures along the 100°C isotherm should accordingly be consistently known to a part in 2000 to secure about a three per cent accuracy in B_0.

Figure 1 is a diagram containing as ordinates $v(pv/RT - 1)$ values for the 440°C isotherm for steam [1] and densities as abscissae corresponding to 50 cm³/g to 10 cm³/g. The diagram also contains the quantity $v \log (pv/RT)$ a function expressible in terms of the virial coefficients defined by equation (1) as follows,

$$v \log \frac{pv}{RT} = B_0 + (B_1 - \tfrac{1}{2}B_0^2)\frac{1}{v}$$ (1a)

The course of the curves, particularly for $v(pv/RT - 1)$ values, show a pronounced curvature as the ordinate axis is approached. It is of interest to consider what could divert the course of the curves as increasingly large specific volumes come under consideration. Let it be assumed that measurements are conducted
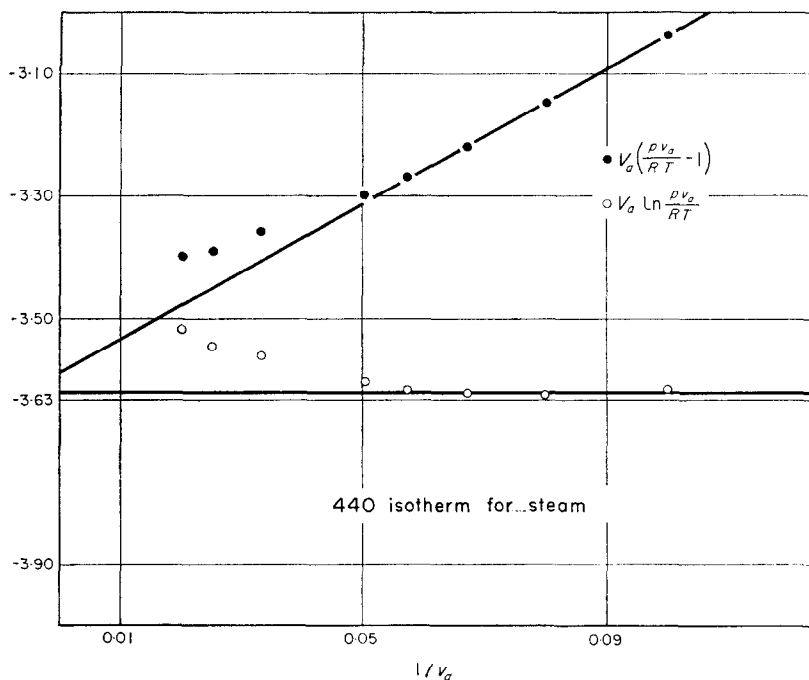
FIG. 1.

in a vessel of invariable volume V, whose surface exposed to the substance being measured is S. The mass increments M_1, M_2, $(M_n = \overset{n}{\underset{1}{\Sigma}} M)$ are injected progressively into the initially heated and evacuated container of volume V, thus the apparent specific volumes become $(V/M_1) = v_{1a}$, $(V/M_2) = v_{2a}, \ldots v_{na}$ at a series of constant temperatures. The corresponding observed pressures p_1, p_2—are recorded and all relevant corrections applied to the sets of data at each temperature. The temperatures should, of course, be expressed on the thermodynamic scale, but at present there is available only the Beattie [2] results from $0°$ to $444·6°C$ international.

The "baking-out" of the container is an important part of the procedure relating to the securing of exact and consistent data for any substance since it is widely known that appreciable amounts of water vapor, carbon dioxide and other substances are adsorbed and in the case of steel, oxygen may be released from the decomposition of surface or dissolved oxides and nitrogen from nitrides also. The adsorbed water vapor can be particularly disturbing if not completely removed, in the case of CO_2 and NH_3* and other water soluble gases.

The case of steam, under p,v,t, measurement is special, because removal of adsorbed water from the container surface is unavailing and the water molecule is probably the most tenaciously held of any substance in the adsorbed state and likewise adsorbed in largest quantity. It therefore becomes of interest to consider the effect of adsorbed water on the accuracy attainable in measurements of the p,v,t, characteristics of steam.

The amount of a substance adsorbed is known to be a function of temperature and the mass adsorbed diminishes rapidly with increasing temperature. At constant temperature the mass adsorbed rises rapidly with pressure to near constancy at relatively low pressure.

* Carbon dioxide or ammonia when introduced into an exhausted globe will dissolve in the adsorbed water layer. This circumstance emphasizes the desirability of "baking out" the container to be used subsequently for p,v,t, measurements.

Qualitatively, therefore, it is perceived that the effect of adsorption will be important at low gas densities and particularly in the case of the water molecule. Some notion of the quantitative effect may be obtained from observations of Irving Langmuir* who found that, after exhausting a glass vessel of 161 cm² surface to a very high vacuum at room temperature, on heating to 360°C, $2\cdot41 \times 10^{-4}$ g of water vapor was released from the glass surface, say, $1\cdot5 \times 10^{-6}$ g/cm². At 100°C and under saturation pressure the specific volume of steam is 1673·5 cm³. A sphere of the latter volume would have a surface of 678 cm² and on the basis of $1\cdot5 \times 10^{-6}$ g/cm² adsorbed water, covered with $678 \times 1\cdot5 \times 10^{-6}$ or 1.10^{-3} g of water vapor; a minimal amount equal to about 0·1 per cent of the (glass) globe contents. However, at saturation pressure the surface adsorbed would be $0\cdot1 \times n$ per cent where n could easily be 2 to 10.

Having obtained p,v,t, data by the procedure sketched above its correlation can conveniently begin by computing the quantity

$$v_a \left(\frac{pv_a}{RT} - 1 \right) = B_{0a} + B_{1a} \frac{1}{v_a} \qquad (2)$$

where v_a is the apparent specific volume or $v_a = V/M$ uncorrected for adsorption. Let $s(p,t)$ represent the mass adsorbed per unit area in a specified container. Then $s(p,t)S$ will be the actual mass adsorbed at a specified temperature and pressure for the container whose working volume is V,† and whose corresponding surface in contact with the vapor is S. Then $s(p,t)S/M$ or σ is the adsorbed amount per unit mass of material contained in a vessel at specified pressure and temperature.

The unaffected specific volume, v, will accordingly be

$$v = \frac{V}{M - s(p,t)S} = \frac{v_a}{1 - \sigma} \qquad (3)$$

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* Langmuir many decades ago (1913) measured the water vapor evolved from a glass bulb highly evacuated at room temperature. The amount of water given up by the surface at 360°C amounted to $2\cdot4 \times 10^{-4}$ g or $1\cdot5 \times 10^{-6}$ g/cm².

† The volume of the adsorbed condensed phase is neglected relative to the container volume.

The virial coefficients are defined by equation (1) where v is the exact and unaffected specific volume of the gas.

In the absence of adsorption the expression (2) with v substituted for v_a will give B_0 assuming accurate mass–pressure–volume measurements. In the actual case, $v = v_a/(1 - \sigma)$, we may write,

$$v \left(\frac{pv}{RT} - 1 \right) = v_a/(1 - \sigma) \left(\frac{pv_a/(1 - \sigma)}{RT} - 1 \right)$$

$$= v_a \left(\frac{v_a}{RT} - 1 \right) + \left[\frac{pv_a}{RT}(2 + \sigma) - 1 \right] v_a \sigma \qquad (4)$$

where the quantity

$$v_a \left(\frac{pv_a}{RT} - 1 \right) = B_{0a} + B_{1a} \frac{1}{v_a} +$$

refers to the apparent coefficients. We may then write approximately,

$$B_0 + B_1 \frac{1}{v} = B_{0a} + B_{1a} \frac{1}{v_a}$$

$$+ \left[\frac{pv_a}{RT}(2 + \sigma) - 1 \right] v_a \sigma \qquad (4a)$$

The second term of the right hand member of (4) follows the sign of B_0 which will be positive or negative depending on the temperature. In any case, B_0 and B_1 are pure temperature functions, negative for steam throughout the region or existing data, namely 30–700°C. It will be seen from the diagram Fig. 1 that $v_a[(pv_a/RT) - 1]$ tends to be increasingly too large relative to the values on the straight line vertically under the data at densities corresponding to 20, 30, 40, and 50 cm³/g. It will also be noted that the quantity $v\sigma$, the factor of the adsorption term varies inversely as M^2, the mass in the container. Thus the accelerating aspect of the $v_a[(pv_a/RT) - 1]$ as the density diminishes is forecast.

The advantage of employing the function $v_a \ln (pv_a/RT)$ in place of $v[(pv_a/RT) - 1]$ is brought out in Fig. 1 by the course of data in relation to the density. The values of $v_a \ln (pv_a/RT)$ at 10 cm³/g namely $-3\cdot62$, at 12·5, $-3\cdot624$ at 15, $-3\cdot622$, at 17·5, $-3\cdot616$, at 20, are nearly constant and nearly equal to the extrapolated value of B_0 namely $-3\cdot63$ given by the closed expression,

$$B_0 = 2\cdot062 - 2901\cdot7\tau \times 10^{7\cdot424 - 10^4\tau^2} \quad [3]$$

Of course the latter equation was based on the data of reference [1] correlated by employing the function $v \ln (pv/RT)$ [4].

Should adsorption be the essential cause of the curvature of the $v_a[(pv_a/RT) - 1]$ or $v \ln (pv_a/RT)$ isotherm values as small densities are approached the differences in $v[(pv/RT) - 1]$ and $v_a[(pv_a/RT) - 1]$, equation (4) and (4a), namely approximately $v_a\sigma$, should vary in proportion to v_a or σ should be approximately constant. Taking the differences between the experimental values of $v_a[(pv_a/RT) - 1]$ and the similar value on the straight line vertically below we may calculate σ. Thus at 50 cm³/g σ is $2·5 \times 10^{-3}$, at 40 cm³/g, $2·5 \times 10^{-3}$, at 30 cm³/g, $2·5 \times 10^{-3}$; larger than $1·1 \times 10^{-3}$ derived from Langmuir's data on the vacuum adsorption of water vapor on glass as would be anticipated.

An example of the application of equation (1) may be cited for steam at 100°C and saturation where the true value of $v[(pv/RT) - 1]$ is 1673·5 [(1/1·0156) - 1] = -26·1, using the adsorption of water vapor on glass found by Irving Langmuir cited above, namely $1·0 \times 10^{-3}$ g, for the surface of a 1573 cm³ spherical container. The adsorption for 1 atm of water vapor at 100°C may be set equal to $n \times 1 \times 10^{-3}$ g where n would undoubtedly be a multiple of unity. We find for the second term right-hand member of (4) [0·97] 1·673 $\times \sigma \times 10^{-3} \times n = 1·6n$. The value of $v[(pv/RT) - 1]$ given above is -26·1 and $v_a[(pv_a/RT) - 1]$ becomes $-26·1 + 1·6n$ or a considerable error is involved should n equal unity. In the case of steam the amount actually adsorbed at 1 atm and 100°C would be a maximum since the saturation line has been reached.

During the course of the earlier p,v,t, measurements [1] it was not found possible to obtain consistent p,v,t, data below 200°C. As a consequence it was not until 1938 [5] that measurements of $(\partial h/\partial p)_T$ were reported for the range 40–125°C which provided values from which the second virial coefficients for steam at the five temperatures 38·9, 59·44, 80·02, 100 and 125 may be deduced. It will be noted that the measurement of $(\partial h/\partial p)_T$ or $v - T(\partial v/\partial T)$ yields values unaffected by adsorption.

The measurements of $(\partial h/\partial p)$ extrapolated to zero pressure yields values of $(\partial v\tau/\partial \tau)$ where

τ is the symbol for $1/T$ and

$$\frac{\partial v\tau}{\partial \tau} = v + \tau \frac{\partial v}{\partial \tau} = v - T \frac{\partial v}{\partial T}$$

As p approaches zero $v = (RT/p) + B_0$ from equation (1) and

$$\frac{\partial v\tau}{\partial \tau} = \frac{\partial B_0\tau}{\partial \tau} = v - T \frac{\partial v}{\partial T}$$

Accordingly for p approaching zero,

$$\frac{\partial v\tau}{\partial \tau} = \left(\frac{\partial h}{\partial p}\right) = \frac{\partial B_0\tau}{\partial \tau} \qquad (5)$$

From the experience with the earlier p,v,t, data [1, 3] it was found that the B_0 values could be well represented by the closed expression,

$$B_0 = \beta - c\tau . 10^{\bar{c}_2\tau^2}$$

Using this expression we find for $p \to 0$:

$$\left(\frac{\partial h}{\partial p}\right)_T = \frac{\partial B_0\tau}{\partial \tau} - \beta - 2c\tau . 10^{\bar{c}_2\tau^2} (1 + c_2\tau^2) \quad (6)$$

Transforming (6) the following relation results,

$$z = \frac{[-(\partial h/\partial p)_T + \beta]T}{(1 + c_2\tau^2)} = 2c . 10^{\bar{c}_2\tau^2} \qquad (7)$$

Accordingly if a diagram employing log z and τ^2 is formed in the case of steam employing the data for $(\partial h/\partial p)_T$ [5], a linear relationship Fig. 2 should result. $\beta = 2$ cm³/g may be employed and $c_2 = 17·09 . 10^4$ from reference [3].

The Fig. 2 indicates that $2c$, the coefficient in equation (7) (Paper VII) [3] is 6123 and $\bar{c}_2$ (base 10) $7·126 \times 10^4$. This compares with 5804 from $(\partial B_0\tau/\partial \tau)$ using the value $2c = 5804$ and $\bar{c}_2 = 7·243 \times 10^4$ from the (Table 1) B_0 obtained from the earlier p,v,t, data.* Table 1 contains the values of $(\partial h/\partial p)$ calculated from the constants of the equation of the straight line through the log z; τ^2 data of Fig. 2. The Keyes–Smith–Gerry values of the third row in

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* The value $\bar{c}_2 = 7·126 . 10^4$ found from z [equation 8] could be employed to obtain a second approximation from the original $(\partial h/\partial p)$ data. However, $7·126 . 10^4$ seems to be consistent with the precision of the original $\partial h/\partial p$.

$$\log Z = \log\left[-\frac{T\left(\frac{\delta h}{\delta p} - \beta\right)}{(1 + c_2 r^2)}\right]$$

○ C.K.(5)
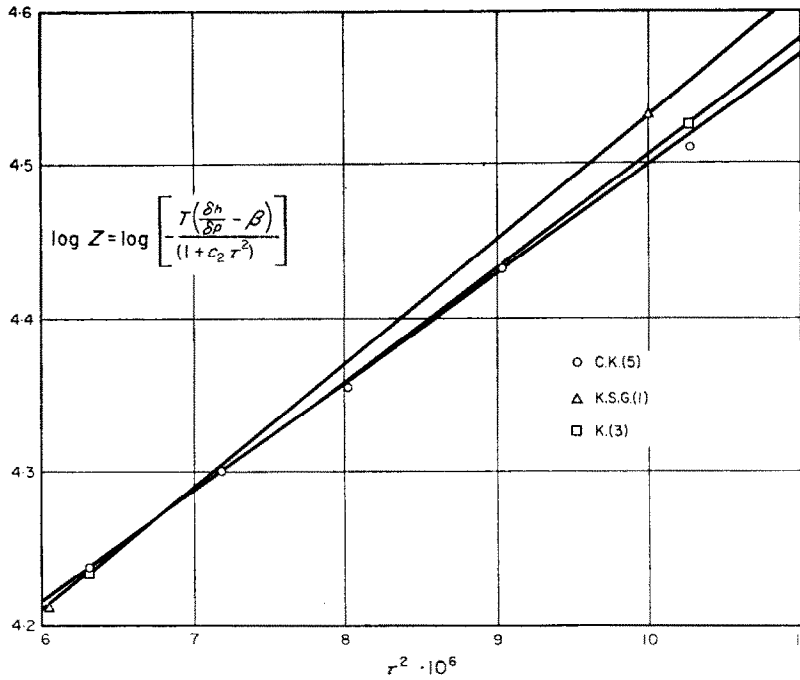
△ K.S.G.(1)

□ K.(3)

$r^2 \cdot 10^6$

FIG. 2.

Table 1 are from the B_0 equation [1] originally formulated from the K–S–G data using the relation $v[(pv/RT) - 1]$. The fourth line is from Steam Paper VII [3] based on the same data as the K–S–G 1936 equation of state (Keenan and Keyes Steam Table, equation 13, p. 15) but employing the $v \ln (pv/RT)$ extrapolation procedure.

Table 1. *Measured values of* $(\partial h/\partial p)$ *for zero pressure and comparisons computed from first virial coefficients derived from p,v,t, data*

				Units cm³/g int. atm.				
Temperature	38·94	59·44	80·02	100	125	2A/R	$\bar{c}_2 . 10^4$	
$(\partial h/\partial p)_T$ obs.	284·9	205·1	150·0	117·2	88·0			
$(\partial h/\partial p)_T$ equation of obs.†	281·9	199·5	147·6	114·1	86·1	6123	7·126	
$(\partial h/\partial p)_T$ K–S–G*	331·5	227·5	164·0	124·1	91·5	5283	8·087	
$(\partial h/\partial p)_T$ Keyes 1949 [3]	294·2	206·2	151·3	116·2	87·0	5804	7·424	
B_0 equation of obs.†	50·9	38·6	30·3	24·7	19·7			
B_0 K–S–G 1936	55·3	40·8	31·4	25·1	19·5			
B_0 Keyes 1949	51·7	38·9	30·4	24·5	19·1			
Saturation Volume	20039	7867	3394	1673·4	770·4			
$100[B_0/v_{sat}]$	0·258	0·494	0·893	1·46	2·52			

* Keyes, Smith and Gerry [1]

† The tabulated values correspond to the line drawn through the observed data entered on Fig. 2.

B_0 values "equation of obs." are calculated from the c and $\bar{c}_2$ derived from the equation for the observed data, line 2.

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Résumé—On explique la non-linéarité des valeurs expérimentales isothermes de $v(pv/RT - 1)$ et $v \ln (pv/TR)$, quand on est en présence de pressions de vapeur faibles, par l'adsorption de l'eau sur les parois du réservoir. La valeur connue de l'adsorption de la vapeur d'eau sur le verre est en bon accord avec l'évolution aux basses pressions des quantités $v(pv/RT - 1)$ et $v \ln (pv/RT)$ et les relations quantitatives pour l'isotherme 440 de la vapeur sont tout à fait satisfaisantes. Pour la détermination du second coefficient du viriel, la supériorité de la fonction d'extrapolation $v \ln (pv/RT)$ est mise en évidence. Les avantages des mesures de $(\partial h/\partial p)$ pour la détermination des coefficients du viriel, indépendamment des perturbations dues à l'adsorption, sont notés et les résultats obtenus, comparés aux coefficients du viriel déduits des données p,v,t.

Zusammenfassung—Die Adsorption von Wasser an den Behälterwänden wird herangezogen, um den nichtlinearen Verlauf der isothermen Versuchswerte von $v(pv/RT - 1)$ und $v \ln (pv/RT)$ bei kleinen Dampfdichten zu erklären. Es ist festzustellen, dass die bekannte Grösse der Wasserdampfadsorption an Glas in Übereinstimmung mit dem Verhalten der Grössen $v(pv/RT - 1)$ und $v \ln (pv/RT)$ bei kleiner Dichte ist und dass die quantitativen Beziehungen für die 440°C—Isotherme von Wasserdampf befriedigend sind. Zur Bestimmung des zweiten Virialkoeffizienten wird die Überlegenheit der Extrapolationsfunktion $v \ln (pv/RT$ gezeigt. Die Vorteile der $\partial h/\partial p$—Messungen zur Ableitung von Virialkoeffizienten, die frei von Störungen durch Adsorption sind, werden erläutert und Vergleiche mit aus pvt-Werten abgeleiteten Virialkoeffizienten angestellt.

Аннотация—Для объяснения нелинейной зависимости экспериментальных значений $v(pv/RT-1)$ и $v \ln (pv/RT)$ для изотермических процессов при малых давлениях пара использовано явление адсорбции воды на стенках контейнера. Отмечено, что существующая величина адсорбции водяного пара на стекле соответствует значению величин $v(pv/RT-1)$ и $v \ln (pv/RT)$ при низкой плотности, и, действительно, количественные соотношения, полученные для 440°С изотермы пара, дают удовлетворительные результаты. Показано превосходство экстраполяционной функции $v \ln (pv/RT)$ для определения второго вириального коэффициента. Проиллюстрировано преимущество метода измерения $(\partial h/\partial p)$ с целью вывода вириальных коэффициентов, свободных от влияния адсорбции, и сделаны сравнения с вириальными коэффициентами, выведенными из значений параметров p, v и t.