Adsorption and Molecular Association in the Burnett Apparatus

Physical adsorption errors accumulate in the isothermal Burnett *PvT* apparatus. The equations describing this sequential phenomena plus diagnostic methods and correction procedures are given. Shift of the apparent volume ratio, the principal indication of significant adsorption, is related to the difference between the surface and volume ratios. The effect of adsorption on the usual Burnett graphs follows from real and simulated data examples. Isochoric coupling as related to the adsorption problem is fully reviewed.

Experiences with chemisorption are related and explained for the first time. Molecular association, which is properly measured by the Burnett apparatus, is compared to adsorption where the two phenomena coexist.

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SCOPE

The Burnett method is widely used by experimentalists to measure gas densities on isotherms. Repeated expansion of the gas from a primary volume into a previously evacuated secondary volume produces an isothermal pressure sequence from which the corresponding density sequence is calculable without experimental volume determination. Experimental errors such as those due to adsorption accumulate with each expansion.

This paper is a comprehensive guide for the experimentalist to the adsorption problem which often plagues the Burnett apparatus at subcritical temperatures. Correlators compiling thermodynamic property tables may find the work valuable in their critical evaluation of a *PvT* data set where adsorption is suspect.

Our objectives were to develop the theoretical equations coupling adsorption with the Burnett method to provide a scientific base for diagnosis and corrective procedures. The latter, which may be classified as changes in apparatus design and variations of the data procurement method, are based on our experience with highly polar vapors which tend to exhibit strong physical adsorption and molecular association at low reduced temperatures.

Two previous developments are noteworthy: (1) recognition in 1968 (Anderson et al.) of the shift of the apparent apparatus constant as a diagnostic tool for adsorption and (2) the emergence in 1972 (Pope et al.; Hall and Eubank) of isochoric coupling as a variation of the Burnett method for minimization of adsorption error.

CONCLUSIONS AND SIGNIFICANCE

Adsorption is shown to affect Burnett *PvT* data even when the gas is perfect. Shift of the apparent apparatus constant is in practice a necessary and sufficient criterion for adsorption. The presence of curvature at low pressure in the standard Burnett graphs is shown to be a deceptive criterion. A prime adsorber, such as an expansion valve packing, produces greater adsorption errors when in the secondary volume. In a simulated problem with 15% adsorption, significant deviations from the correct compressibility factors and second virial coefficient result. Isochoric coupling is shown to reduce these errors to within usual experimental precision.

Chemisorption is easily diagnosed by failure to equilibrate. An apparatus which has suffered chemisorption must be resurfaced and calibrated. Molecular association, which does not significantly lengthen equilibration times, is correctly measured by the Burnett apparatus where adsorption is absent.

Whenever *PvT* measurements are made on pure vapors at subcritical temperatures, physical adsorption of the molecules to the inner walls of the container must be considered as a possible error source. Due to the sequential nature of isothermal Burnett data (Burnett, 1936), adsorption errors accumulate; every expansion creates a deviation from the fundamental assumption of Burnett data reduction; the number of free or unadsorbed molecules are conserved upon each expansion. A vapor which produces an adsorption error of 0.01% in the density at a given pressure and temperature with a conventional single cell or isochoric apparatus can easily provide errors of one or even two orders of magnitude higher in a Burnett apparatus where each run consists of ten expansions. The problem is then to first diagnose the presence of adsorption errors in the data and second to eliminate or diminish their effect. The latter phase, the treatment, takes three forms:

1. Revise the apparatus by changing the surfaces which contact the experimental gas,

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2. Change the data procurement procedure (that is, combine the Burnett and isochoric methods or abandon the Burnett method), and

3. Attempt to correct the Burnett data by estimation of adsorption contributions.

The last treatment is complicated since the pressure exerted by a gas at a given temperature and amount of charge to the container is a function of both the compressibility of the gas and its tendency to adsorb to the surrounding surface. Both phenomena clearly reduce the observed pressure so the correction scheme must successfully sort out the contribution of each. Independent measurement of the amount of adsorption would solve the problem, of course, but how is such a determination to be made? We must use the same surface (that is, the particular Burnett apparatus) so increase-in-weight methods seem impractical and pressure measurement procedures depend on accurate knowledge of the gas compressibility.

This paper will consider diagnosis and the three methods of treatment of physical adsorption errors with the Burnett apparatus. The diagnoses and prevention of chemisorption (which generally leads to no Burnett data due to failure to equilibrate) will also be discussed. Molecular association and the use of the Burnett apparatus with highly polar vapors such as water and alcohols will be reviewed. It should be emphasized that interactions between free gas molecules under equilibrium conditions are part of the compressibility of a compound and thus properly measured in a Burnett apparatus with no corrections required—indeed, association constants and the fraction of various polymers present are often estimated from virial coefficients as by Lambert et al. (1949). We exclude chemical reactions that produce new monomeric species, however, from the above statement. For example, suppose the equilibrium composition of ethanol at a given pressure and temperature is 95% monomer and 5% dimer due to hydrogen bonding. Perhaps arbitrarily, the correct compressibility factor of ethanol is considered to be that of this mixture whereas fractions of water plus ethylene present in chemical equilibrium with ethanol would constitute impurities. Since molecular association equilibrium times are usually short and well within the Burnett equilibration time of a few hours whereas uncatalyzed chemical decomposition rates are usually immeasurably slow for stable compounds near ambient conditions, the Burnett or any PvT apparatus will equilibrate and yield results reproducible by other laboratories. Adsorption, however, leads to data which cannot be reproduced by any apparatus but the original since the duplication of surface size, smoothness, and other characteristics is virtually impossible.

PHYSICAL ADSORPTION THEORY

Before we attempt to diagnose or treat the adsorption problem, a general theory of adsorption coupled with the Burnett method will be reviewed. No specific models, whether the PvT equation of state or the adsorption isotherm, will be assumed initially.

Prior to the $(i + 1)$ Burnett expansion

$$P_i V_A = Z_i n_i RT \qquad (1)$$

and after

$$P_{i+1}(V_A + V_B) = Z_{i+1} n_{i+1} RT \qquad (2)$$

Due to adsorption, n_i does not necessarily equal n_{i+1}, but rather

$$n_i + (m_A)_i = n_{i+1} + (m_A + m_B)_{i-1} \qquad (3)$$

Substitution of the free gas mole ratio (n_{i+1}/n_i) of Equation (3) into the ratio of (2) by (1) yields

$$(P_{i+1}/P_i)N = (Z_{i+1}/Z_i)\left[1 + \frac{(m_A)_i - (m_A + m_B)_{i+1}}{n_i}\right] \qquad (4)$$

For a given isothermal expansion, m_A and m_B are each a function only of pressure or $m_A = f_A(P)$ and $m_B = f_B(P)$. If the adsorption is strictly physical, $f_A(0) = 0$ and $f_B(0) = 0$. For moderately low pressures, expansion of these functions into Taylor series about $P = 0$ provides

$$f_A(P) = \sum_{j=1} f_A{}^{(j)}(0) \cdot [P^j/j!] \qquad (5)$$

and likewise for $f_B(P)$. Combination of the last two equations and substitution of Equation (1) for n_i yields finally

$$\frac{P_{i+1}}{P_i} = \frac{\left(\frac{Z_{i+1}}{Z_i}\right)\left[1 + \frac{Z_i RT}{V_A}\left[\sum_{j=1} f_A{}^{(j)}(0) \cdot [P_i{}^{j-1}/j!]\right]\right]}{N + (Z_{i+1}RT/V_A)\sum_{j=1}[f_A{}^{(j)}(0) + f_B{}^{(j)}(0)][P_{i+1}^{j-1}/j!]} \qquad (6)$$

Most important is the zero pressure limit of the pressure ratio, the apparent volume constant,

$$U_0 \equiv \lim_{P_i \to 0}\left[\frac{P_i}{P_{i+1}}\right] = \frac{N + (RT/V_A)\,[f_A{}^{(1)}(0) + f_B{}^{(1)}(0)]}{1 + (RT/V_A)\,[f_A{}^{(1)}(0)]} \qquad (7)$$

If we ignore cell distortions with pressure, $(RT/V_A) \equiv \alpha_A$ is constant or

$$U_0 = \frac{N + \alpha_A[f_A{}^{(1)}(0) + f_B{}^{(1)}(0)]}{1 + \alpha_A[f_A{}^{(1)}(0)]} \qquad (8)$$

There are two cases when $U_0 = N$. The first is for $f_A{}^{(1)}(0) = f_B{}^{(1)}(0) = 0$, but adsorption isotherms are usually convex upwards and do not exhibit zero slope at zero pressure. The second is for $[f_A{}^{(1)}(0) + f_B{}^{(1)}(0)]/f_A{}^{(1)}(0)$ to equal N. To gain a better physical understanding of this condition, we define the surface ratio

$$(S_R)_i \equiv \left(\frac{S_A + S_B}{S_A}\right)_i \equiv \left(\frac{m_A + m_B}{m_A}\right)_i \qquad (9)$$

When the adsorption isotherms of both A and B are linear with pressure $(S_R)_i$ is independent of pressure. Application of L'Hopital's rule yields

$$\lim_{P_i \to 0}(S_R)_i \equiv S_{R0} = \frac{f_A{}^{(1)}(0) + f_B{}^{(1)}(0)}{f_A{}^{(1)}(0)} \qquad (10)$$

Thus the case of $S_{R0} = N$ results in the usual relation for nonadsorbing gases of $N = U_0$. The apparent apparatus constant will shift from the true value by

$$(U_0 - N) = K_A(S_{R0} - N)/(1 + K_A) \qquad (11)$$

The classical procedure for extraction of compressibility factors from Burnett data relies on the equation

$$\lim_{P_i \to 0} P_i N^i = (P_0/Z_0) \tag{12}$$

Equation (6) yields only

$$\left(\frac{P_0}{Z_0}\right) = \left(\frac{P_i}{Z_i}\right) \prod_{k=0}^{i-1} \left[\frac{N + Z_{k+1}\alpha_A \left[\sum_{j=1} [f_A^{(j)}(0) + f_B^{(j)}(0)] \right] [P_{k+1}^{j-1}/j!]}{1 + Z_k\alpha_A \sum_{j=1} [f_A^{(j)}(0)][P_k^{j-1}/j!]} \right] \tag{13}$$

a general but discouraging result. When adsorption is linear with pressure on both surfaces, the equation is more palatable

$$\left(\frac{P_0}{Z_0}\right) = \left(\frac{P_i}{Z_i}\right) \prod_{k=0}^{i-1} \left(\frac{N + Z_{k+1}K_A S_{R0}}{1 + Z_k K_A} \right) \tag{14}$$

Only when $S_{R0} = N$ does the argument of the product approach N as $P \to 0$. For Equation (12) to be valid S_{R0} must equal $N(Z_k/Z_{k+1})$ for all k. As S_{R0} and N are fixed, this condition is possible only for a perfect gas. If $S_{R0} = N$, Equation (14) reduces to

$$(P_0/Z_0) = (P_i/Z_i)N^i \left[\frac{1 + Z_i K_A}{1 + Z_0 K_A} \right] \tag{15}$$

PHYSICAL ADSORPTION DIAGNOSTICS

The above equations show that except for the case of linear adsorption with $S_R = N$ for a perfect gas, adsorption changes the pressure sequence and is cumulative. A trivial exception is the unlikely case that the molecules adsorb on V_A at the initial pressure P_0, stay on A during the entire course of the Burnett run, and no molecules adsorb on B. This would only decrease the values in the pressure sequence but would not cause error in the compressibilities.

As physical adsorption equilibration times are generally less than the usual thermal equilibration times following an expansion, a prolonged drop in pressure ($S_{R0} > N$) or increase ($S_{R0} < N$) is not observed. Equation (11) provides then the simplest test for adsorption. The true volume constant N is known from the helium or nitrogen calibration data. Extrapolation of the pressure ratios of the experimental gas to zero pressure yields the apparent volume constant U_0. If adsorption is unimportant, the value of K_A will be so small that $U_0 \cong N$ regardless of the surface-to-volume ratio S_{R0}/N. When adsorption is important, U_0 will exceed N if $S_{R0} > N$ or strong adsorption occurs in V_A. If V_A and V_B were simple capped cylinders or simple spheres ($V_A > V_B$), the surface-to-volume ratio would exceed unity and $U_0 > N$. In practice with tubing, valves, and pressure transmission devices associated with the volumes V_A and V_B, the surfaces S_A and S_B are composite and different. Particularly when the pressure is measured in V_A with a differential pressure indicator, the surface-to-volume ratio can fall below unity as for the data of Anderson et al. (1968). Final evidence that adsorption is important is the approach of U_0 to N as temperature increases. Physical adsorption diminishes with temperature and, hopefully, is not an important source of error for the maximum isotherm of the particular investigation.

For practical purposes a shift of the volume constant $U_0 - N$ is a necessary and sufficient criterion for the presence of adsorption. In the somewhat unlikely event that $S_{R0} = N$, it is obviously not a necessary condition. The adsorption will then go undetected but alters the pressure sequence and compressibilities as seen from Equation (15) even for linear adsorption.

A prime adsorber in V_A will cause $S_{R0} = 1$ whereas a prime adsorber in V_B yields $S_{R0} = \infty$. The apparent volume constant thus has a lower but no upper bound for a given isotherm.

We now examine the usual Burnett graphs of (P_i/P_{i+1}) versus P_i and P_iN^i versus P_i to see changes caused by adsorption. Figure 1 illustrates the shift of the volume constant for the simple case of linear adsorption of a perfect gas where Equation (6) reduces to

$$(P_i/P_{i+1}) = N\left[\frac{1 + K_A(S_R/N)}{1 + K_A} \right] \tag{16}$$

The pressure ratio is thus independent of pressure.

Figure 2 shows that the pressure ratio is linear with pressure for a second Berlin virial coefficient gas

$$Z = 1 + B_pP \tag{17}$$

with no adsorption (curves 1 and 4). Linear adsorption with $S_R = N$ causes increasing departure from these curves with pressure (curves 2 and 3) but the same intercept N. Curves 6 and 5 are the analogous results when $S_R < N$; vertical displacement of these two curves to an intercept U_0 above N would result for $S_R > N$ (not shown). The nature of these curves is found by examination of

$$(P_i/P_{i+1}) = (Z_i/Z_{i+1})N\left[\frac{1 + Z_{i+1}K_A(S_R/N)}{1 + Z_iK_A} \right] \tag{18}$$

the general relation for linear adsorption from Equations (6) and (17). The results of Figure 2 are representative of what occurs to real gases at low and moderate pressure. As the pressure drops, the curvature decreases for a real gas without adsorption as Equation (17) is approached. Comparison of curves 3 and 4 illustrates the curvature caused by adsorption. The *presence* of curvature at low pressures is a deceptive criterion for adsorption because the curvature (curve 3) could have been

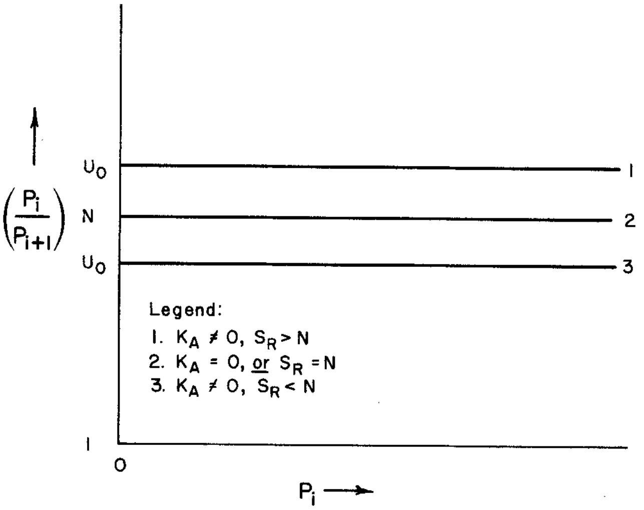

Fig. 1. Typical Burnett pressure ratios with linear adsorption of a perfect gas.

caused by significant contributions from virial coefficients higher than the second. A positive criterion would be increasing curvature with decreasing pressure but Equation (18) and the experimental evidence of Kerns (1972) do not support this hypothesis (Waxman and Hastings, 1971). The reason is that the adsorption isotherms are similar in nature to the compressibility factor isotherms and both approach linearity as pressure approaches zero. Nonlinearity of the adsorption isotherm will, of course, increase the curvature (of curve 3), but this effect will fade as pressure approaches zero. Finally, Figure 1 illustrates that adsorption does not increase the curvature at low pressures for a perfect gas.

It should not be implied from Figure 2 that the slope at zero pressure is the same for curves 3, 4, and 5. Indeed, the slope of curve 4 is $B_p(N - 1)$ whereas that of curve 3 is $B_p(N - 1)/(1 + K_A)$. The general relation for the zero pressure slope with linear adsorption is

$$\frac{B_p\left[(N-1) + K_A(N+1)\left(\frac{S_R}{N} - 1\right)\right]}{1 + K_A\left(2 - \frac{S_R}{N}\right)}$$

Thus, curves 4, 3, and 5 have progressively less (negative) slope at $P = 0$.

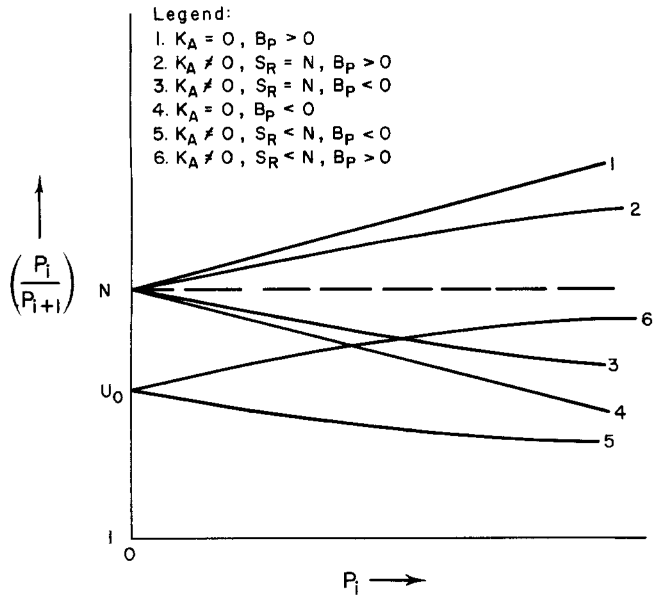

Fig. 2. Typical Burnett pressure ratios with linear adsorption of a second Berlin virial coefficient gas.

Figure 3 is for a Dieterici gas undergoing simulated adsorption for a Burnett isotherm of 150°C as reported by Hall and Eubank (1972). The constants for the Dieterici equation of state

$$[P \exp(a/vRT)](v - \bar{b}) = RT \qquad (19)$$

were calculated from the critical constants of methanol as $a = 1.18027 \times 10^3$ m^5/kg-s^2 and $\bar{b} = 2.2220 \times 10^{-3}$ m^3/kg. Reasons for the use of the Dieterici equation were (1) simplicity, (2) closed form, (3) reasonable value of Z_c of 0.270, and (4) temperature dependent virial coefficients. Adsorption was simulated with $S_R = 1.10$, $N = 1.40$, and $U_0(150°\text{C}) = 1.35$. The adsorption isotherm was assumed to be linear with a slope, $(f_A^{(1)}/V_A) = 1.8215 \times 10^{-6}$ s^2/m^2 calculated from Equation (11) and the shift of the volume con-

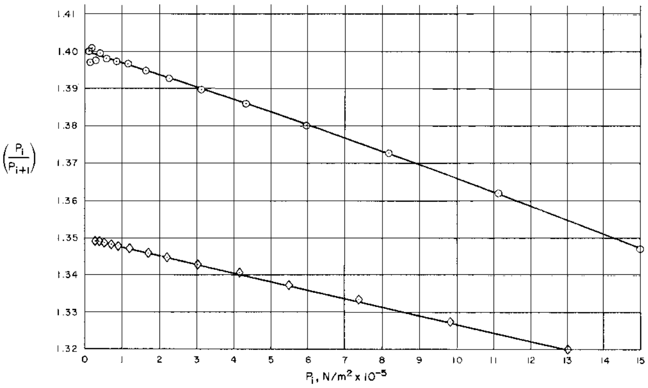

Fig. 3. Burnett pressure ratio for simulated Dieterici gas example. ⊙ Linear Adsorption. ◈ No Adsorption.

TABLE 1. SIMULATED BURNETT DATA WITH ADSORPTION (150°C)

Linear adsorption ($N = 1.40$, $U_0 = 1.35$, $\rho_0^* = 15.832$ kg/m^3)				No adsorption ($N = U_0 = 1.40$, $\rho_0 = 15.832$ kg/m^3)		
P_i, N/m^2 × 10^{-5}	P_i/P_{i+1}	P_iN^i	$P_iU_0^i$	P_i, N/m^2 × 10^{-5}	P_i/P_{i+1}	P_iN^i
13.161	1.3194	13.161	13.161	15.199	1.3475	15.199
9.9749	1.3276	13.965	13.466	11.279	1.3622	15.792
7.5134	1.3336	14.727	13.528	8.2803	1.3729	16.228
5.6341	1.3379	15.460	13.861	6.0312	1.3804	16.549
4.2111	1.3411	16.178	13.987	4.3691	1.3861	16.784
3.1400	1.3426	16.888	14.080	3.1521	1.3901	16.953
2.3373	1.3452	17.598	14.148	2.2676	1.3928	17.073
1.7375	1.3464	18.317	14.200	1.62810	1.3947	17.162
1.2905	1.3474	19.045	14.237	1.16731	1.3968	17.227
0.95779	1.3480	19.789	14.266	0.83573	1.3972	17.267
0.71051	1.3485	20.552	14.286	0.59815	1.3980	17.302
0.52687	1.3489	21.336	14.301	0.42787	1.3995	17.327
0.39059	1.3492	22.140	14.313	0.30574	1.3977	17.334
0.28950	1.3494	22.977	14.321	0.21875	1.4011	17.362
0.21454	1.3496	23.839	14.327	0.15613	1.3970	17.350
0.15896	1.3496	24.728	14.331	0.11176	—	17.386
0.11775	—	25.651	14.331			

[*] ρ_0 is the initial amount of change divided by the volume V_A which is equal to the gas density at the initial pressure P_0 for the case of no adsorption.

stant. About 15% of the molecules are absorbed in V_A decreasing slightly with pressure due to compressibility; this accounts for the considerable departure in Figure 3 from the adsorption-free or correct results. Table 1 provides the pressure sequences obtained with and without adsorption. We shall return to this simulation later for examination of the P_iN^i diagram and virial coefficients.

Graphs of P_iN^i versus P_i with adsorption are far more difficult to understand or even categorize. What follows is based mostly on experience. First, we recall that

$$P_iN^i = Z_i(P_0/Z_0) \qquad (20)$$

when there is no adsorption so that the *shape* of the P_iN^i versus P_i graph is the same as that of Z_i versus P_i. Figure 4 for acetone at 100°C with N determined from helium is a good example. With an inflection point at about 1.2×10^5 N/m^2 and an apparent asymptotic approach to the P_iN^i axis at zero pressure, this figure hardly bears resemblance to the shape of Z versus P for a subcritical isotherm. The unusual shape of Figure 4 has been observed in cases where S_{R0} is nearly N (that is, adsorption cannot be detected from the shift of the volume constant) and thus provides a secondary method for diagnoses. It was originally believed that the inflection point of Figure 4 was due to nonlinear adsorption, but this appears to be only partially correct. We will illustrate below by the simulation at 150°C that a strong linear adsorption can cause the entire curve to be concave upwards although the true third virial coefficient of the pressure series is strongly negative (-2.805×10^{-15} m^4/N^2). Thus adsorption at low pressure ($\sim$ linear adsorption) makes Figure 4 concave upwards, and the reversal of curvature could follow from the diminished relative importance of adsorption at higher pressures as the slope of the adsorption isotherms decrease (due to the filling of active sites). However, in the case of highly polar gases like acetone, the reversal of curvature is likely more a result of the domination of association at the higher pressures.

The above examples are for $S_{R0} < N$. Recent data for cyclohexane by Kerns (1972) with $S_{R0} > N$ have shown that P_iN^i can exhibit a maximum near zero pressure for low temperatures. Otherwise, the curvature is concave upwards. It should perhaps be emphasized that these interesting but unpleasant shapes have been observed at low pressures and temperatures 200°C below the critical point. They are thus often not observed in laboratories that do not operate at these low reduced temperatures T/T_c or that have only oil dead weight gauges (minimum pressure $\sim 1.4 \times 10^5$ N/m^2).

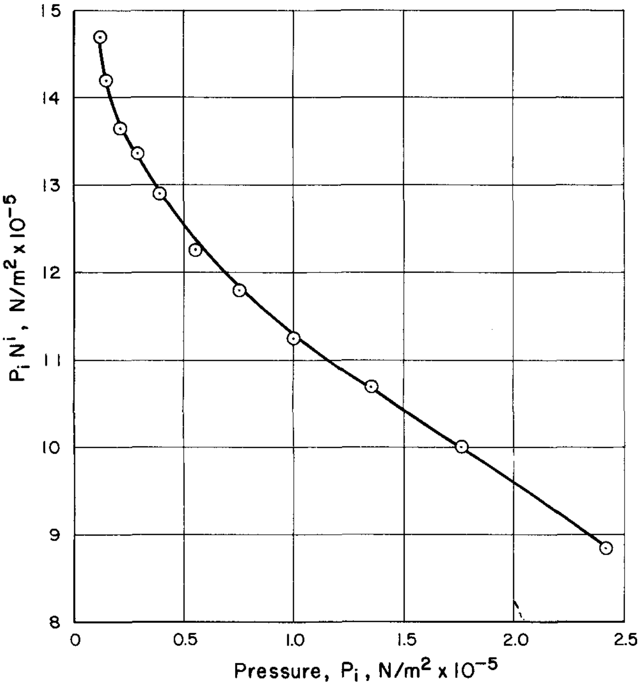

Fig. 4. P_iN^i results for acetone at 100°C (Run III) from Anderson et al. (1968).

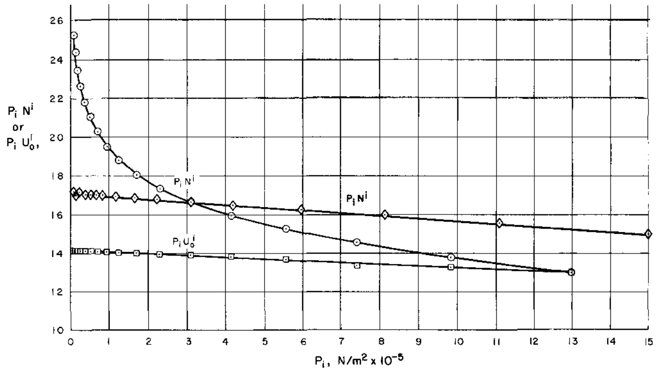

Fig. 5. P_iN^i and $P_iU^i_0$ for simulated Dieterici gas example. ⊙ P_iN^i for linear adsorption with true apparatus constant. ⊡ $P^iU^i_0$ for linear adsorption with apparent apparatus constant. ◈ P_iN^i for no adsorption.

Figure 5 illustrates the concave upward curvature of P_iN^i in the simulated adsorption example at 150°C. The plot of $P_iU_0{}^i$, however, is nearly straight and yields a well-defined intercept at zero pressure. If the value of N is unknown (or equal to U_0), adsorption is not detected from Figure 3 or Figure 5. The compressibility factors and virial coefficients resulting from the $P_iU_0{}^i$ curve are, however, wrong as seen by comparison on Figure 5 with the analogous results in the absence of adsorption. If the zero pressure limit of $P_iU_0{}^i$ of Figure 5 of about 1.435×10^6 N/m^2 is taken as (P_0/Z_0) then $Z_0 = 0.914$ at $P_0 = 1.3161 \times 10^6$ N/m^2 or the second virial coefficient of density, $B_2 = B_p(RT)$, is -5.49×10^{-3} m^3/kg. As noted above the correct value of B_2 is -8.5276×10^{-3} m^3/kg and $Z_0 = 0.894$ at $P_0 = 1.3161 \times 10^6$ N/m^2. Conversely, if $S_R > N(U_0 > N)$, the compressibility factors will be low and $-B_2$ high when computed from $P_iU_0{}^i$.

THE TREATMENT OF PHYSICAL ADSORPTION

As noted in the introduction, there are three categories for methods of attacking the adsorption problem—alter the apparatus, change the data procurement procedure, or correct the Burnett data by estimation of adsorption contributions.

Apparatus Alterations

Adsorption can be reduced by changing the container metal or its surface. Type 303 stainless steel gives a poor finish and should be avoided. Precipitation-hardening grades of stainless, such as 17-4PH or 17-7PH hardened to around 38-40 Rockwell-C, or AISI 440 (grade A, B, or C) are recommended by Myers (1969) for excellent surfaces. The elimination of the usual tapers at the bottom of V_A and V_B is desirable. Finally, the surface of the cell should be *super* finished to minimize area. Processes are available which machine with a diamond tool to produce surfaces better than one micro-in. root mean square.

If these procedures fail, the metal surface can be plated or coated with some other material. Gold plating* offers advantages in the reduction of both physical and chemical adsorption; epoxy and teflon vapor coatings are another possibility as is glass liners. Since as much as one-third of the total surface areas of V_A and V_B exposed to the experimental gas may be outside the principal cells, the refinishing or plating of tubing, valves, and differential pressure indicators must also be considered.

A particular problem is adsorption by the packing in the Burnett expansion valve. (The feed inlet valve on V_A and the exhaust valve on V_B should have their packings turned away from the gas in V_A and V_B.) A porous packing material (such as teflon impregnated with brass for temperatures above 150°C) can provide a strong adsorber in V_A or in V_B, depending on the valve placement. It is not difficult to check a suspected packing; a Burnett run is made with the packing on V_A followed by a run at the same temperature with the packing facing V_B. If the packing is the prime adsorber, $N > S_R$ ($\cong 1$) and $N > U_0$ for the first run whereas $N < S_R$ and $N < U_0$ for the second. As long as the packing is an important adsorber, although not perhaps the only or major one, a significant increase in U_0 should be found. Sometimes it is not possible to find a totally nonadsorbing packing suitable for the temperature range of the investigation; the packing should then face V_A in order that $N > S_R$ for the reasons deduced below. Finally, a bellows valve or a twin-seating needle valve (such as designed by the senior author and built by Ruska Instruments) may be used to prevent contact between the packing and gas.

By changing the packing orientation or the cell (V_A or V_B) through which the pressure is measured, the investigator can alter the surface-to-volume ratio without resorting to the harmful addition of unnecessary surfaces. Given a total amount of volume $V_A + V_B$ and a total amount of surface $S_A + S_B$ what is the optimum surface-to-volume ratio for minimization of adsorption errors? For a perfect gas we have seen that there is no change in the pressure sequence (given P_0 and N) when $S_R = N$. For the same condition to hold with linear adsorption of a real gas, the term $[1 + Z_{i+1}K_A(S_R/N)]/(1 + Z_iK_A)$ of Equation (18) must be unity for all P_i or

$$(S_R/N) = (Z_i/Z_{i+1}) \cong (1 + B_pP_i)/(1 + B_pP_{i+1}) \tag{21}$$

where the last equality is valid only for a Berlin second virial coefficient gas. If B_p is negative and $Z_i < Z_{i+1}$, the optimum value of the surface-to-volume ratio is somewhat less than unity, the average value of (Z_i/Z_{i+1}) for the pressure range involved. Clearly (Z_i/Z_{i+1}) changes with pressure whereas (S_R/N) cannot so there is no single value of (S_R/N) that will produce a pressure sequence identical to that without adsorption. Since B_p is strongly negative for subcritical temperatures, a value of (S_R/N) greater than unity should be avoided. A second reason is that an adsorbing surface when placed in V_B will create greater error in the pressure sequence than when placed in V_A.

To understand the last statement consider the case where the gas is perfect and the only adsorbing surface (that is, the packing of the expansion valve) is first with V_A and second with V_B. When in V_A the surface adsorbs part of the original charge to V_A with a resultant equilibrium pressure P_0. We regard P_0 as a correct value since it is the degassing of the adsorbed molecules $(m_A)_0$ that causes adsorption errors in Burnett data. For linear adsorption Equation (6) reduces to

$$(P_{i+1}/P_i) = (1 + K_A)/(N + K_A) = (\beta/N) \tag{22}$$

For $i = 0$, P_1 is seen to be high as expected. After i expansions, the difference between P_i and its value in the absence of adsorption $(P_i)_{NA}$ is

$$P_i - (P_i)_{NA} = (P_0/N^i)(\beta^i - 1) \tag{23}$$

When the same surface is placed in V_B, however, the surface adsorbs following each expansion and presumably is completely degassed during the exhaust of V_B. Now

$$(P_{i+1}/P_i) = (N + K_A)^{-1} = (\gamma/N) \tag{24}$$

where $f_A^{(1)}(0) = f_B^{(1)}(0)$ as the surface is the same, and

$$P_i - (P_i)_{NA} = (P_0/N^i)(\gamma^i - 1) \tag{25}$$

is negative. The ratio of the pressure error of Equation (23) by (25) is

$$\frac{[P_i - (P_i)_{NA}]_A}{[P_i - (P_i)_{NA}]_B} = \left[\frac{\beta^i - 1}{\gamma^i - 1}\right] = \frac{[(1 + K_A)N]^i - (N + K_A)^i}{N^i - (N + K_A)^i} \tag{26}$$

The absolute value of this ratio is $(N - 1)$ for $i = 1$ and

$$\frac{N^2(2 + K_A)}{2N + K_A} - 1$$

for $i = 2$. With $N = 1.40$, a single expansion causes 2½ times the error in P_1 when the surface is moved from V_A to V_B. If also $\alpha_Af_A^{(1)}(0) = 0.1$, two expansions cause $(0.419)^{-1} = 2.39$ times the error in P_2. This rather formal analysis agrees with the intuitive reasoning that the amount of desorption per expansion is proportional to $(P_i - P_{i+1})$ when the surface is with V_A but the adsorption is proportional to P_{i+1} when the surface is with V_B. The ratio is $(P_i - P_{i+1})/P_{i+1}$ or $(N - 1)$ for a perfect gas, in agreement with Equation (26) for $i = 1$. Unless $N > 2$, the reader should now be convinced that a surface-to-volume ratio greater than unity is undesirable.

Data Procurement Procedures

A combination of the isothermal Burnett method with nonisothermal procedures compatible with the Burnett apparatus can offer additional information for adsorption, diagnoses, and treatment. Isochoric coupling appears the most promising and has been recently considered in detail by Pope et al. (1972) and by Hall and Eubank (1972) although first recognized by Burnett (1963) in connection with measurements in the two-phase region for mixtures. Burnett isotherms and the isochores are presented on Figure 6 with P_{MIN} the minimum pressure capable of measurement by the apparatus. As the temperature drops along an isochore, say ρ_2, the free-gas density $\rho_2{}^h$ will decrease due to adsorption. Thus, $\rho_2{}^1 = \rho_2{}^2 = \ldots = \rho_2{}^h$ only when adsorption is negligible down to T^h. A number of diagnostic schemes appear feasible, three of which are given below:

1. The simplest procedure is to start somewhere (say $\rho_2{}^1$) on the highest temperature isotherm T^1 where adsorption is minimum. Equilibrium is attained with the expansion valve open. The valve is then closed and the temperature reduced (to T^2, for example). The pressure

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* Details may be obtained from M. Waxman, Equation of State Section, NBS, Gaithersburg, Md., or from the senior author.

in V_A (or whichever cell is connected to the pressure measurement system) is measured with the valve closed and then again after it has been opened. If the former pressure P_A is significantly greater than the latter P_{AB} adsorption is important at T^2 and the surface-to-volume ratio is greater than unity. Obviously, the two isotherms should be well spaced, at least 25°, and the test fails if the surface-to-volume ratio is unity. When adsorption is negligible at T^1 and linear at T^2,

$$P_A - P_{AB} = \overline{Z}K_A[P_{AB}(S_R/N) - P_A] \qquad (27)$$

where $\overline{Z}(\overline{P})$. Equation (27) can provide a relation between the constants (S_R/N) and K_A [which can be combined with Equation (11)] at low pressures when $Z = 1$ or can be estimated from literature second virial coefficients.

2. A second test is to check a cycle such as $\rho_1{}^1$, $\rho_1{}^2$, $\rho_2{}^2$, $\rho_2{}^1$. A Burnett expansion is first made from $P_1{}^1$ to $P_2{}^1$ at T^1. V_A is then refilled to $P_1{}^1$ at T^1, the gas cooled to T^2, the expansion made at T^2 after which the valve is closed, and finally the temperature on V_A is increased back to T^1 to check the value of $P_2{}^1$. This method is similar to the first and will not be examined in detail.

3. A severe, general test for the entire ρ-T region of the Burnett data is based on the zero pressure limit of $P_i{}^hN^i$ or

$$\lim_{P_i{}^h \to 0} (P_i{}^hN^i) = \frac{P_0{}^h}{Z_0{}^h} = \rho_0{}^hRT^h \qquad (28)$$

A Burnett isotherm is first run at T^1 starting at $P_0{}^1(\rho_0{}^1)$. Following Figure 6, the starting pressure $P_0{}^2$ of the second isotherm T^2 is found by isochoric cooling from $\rho_0{}^1$ to $\rho_0{}^2$. Each isotherm is thus begun at $\rho_0{}^1$. If there is no adsorption, the zero pressure limits of $(P_i{}^hN^i/T^h)$ will be independent of temperature. This procedure is identical in principle to that of Pope et al. (1972) in that the maximum pressure for each isotherm is isochorically coupled to a pressure in the primary sequence at T^1.

If adsorption is detected, what is the best method for obtaining Burnett data from an apparatus with isochoric capability? It is now clear that Burnett expansions should not be made in the presence of adsorption. Instead of expanding from $P_1{}^3$ to $P_2{}^3$, for example, it is better to increase the temperature from T^3 to T^1, expand from $P_1{}^1$ to $P_2{}^1$ and return to T^3. The pressures $P_1{}^3$ and $P_2{}^3$ still contain adsorption errors, of course, but the accumulation of these errors in the Burnett sequence is eliminated if there is no adsorption at the maximum temperature T^1. For efficiency in gathering data, the analogous process of Hall and Eubank (1972) is recommended: a simple Burnett isotherm is run at T^1 except after each expansion an isochore is run down to either P_{MIN} or the vapor pressure (Figure 6). When adsorption is negligible at T^1,

$$P_i{}^h = Z_i{}^hRT^h[\rho_i{}^1\xi_i{}^h - (m_A/V_A)_i{}^h] \qquad (29)$$

where $\xi_i{}^h$ is obtainable from the helium calibration. With $\rho^1{}_i = N\rho^1{}_{i+1}$ and Equation (5), a proper zero pressure limit of the isothermal pressure ratio $(P^h{}_i/P^h{}_{i+1})$ of N is found. However, Equation (12) is only valid at T^1. If the adsorption is linear at T^h

$$\left(\frac{P_0{}^h}{Z_0{}^h}\right) = \lim_{P_i{}^h \to 0} \left[\frac{P_i{}^hN^i\xi_0{}^h - f_A{}^{(1)}(0)\alpha_AP_0{}^h}{1 - f_A{}^{(1)}(0)\alpha_A}\right] \qquad (30)$$

where $f_A{}^{(1)}(0)$ is evaluated at T^h. Equation (30) shows that Equation (12) is now valid for a perfect gas, however, regardless of the surface-to-volume ratio providing $\xi_0{}^h = 1$.

For direct calculation of virial coefficients by nonlinear regression:

$$\sum_i W_i \left[P^h{}_i - RT^h \sum_{k=1}^{K} B_k \left[\rho^1{}_i\xi^h{}_i - (V^h{}_{A,i})^{-1} \sum_{j=1}^{J} f^{(j)}{}_A(0)\,\Big|_{T^h} (P^h{}_i)^j/j! \right]^k \right]^2 = \text{MINIMUM} \qquad (31)$$

where only h and 1 appear as superscripts. Equation (31) can be solved by linear regression for the virial coefficients, $B_2, B_3, \ldots . B_k$, when adsorption is negligible.

The pressure sequence at 150°C (T^2) generated by the Burnett-isochoric method for the Dieterici gas example may be found in Table 1. In addition to the previous constants, $T^1 = 300°\text{C}$, $\rho_0{}^1 = 15.832$ kg/m^3, and $W_i = 1 = \xi_i{}^h$. A nonlinear regression based on Equation (31) with $K = 4$ and $J = 1$, yields $B_2 = -8.5232 \times 10^{-3}$ m^3/kg (-8.5276×10^{-3}), $B_3 = 3.8588 \times 10^{-5}$ (m^3/kg)^2 (3.9867×10^{-5}), $B_4 = -9.4973 \times 10^{-8}$ (m^3/kg)^3 (-1.1918×10^{-7}), and $(f_A{}^{(1)}/V_A) = 1.821558 \times 10^{-6}$ s^2/m^2 (1.8215×10^{-6}). The correct values are in parenthesis. Since the pressure sequence at 150°C was generated based on linear adsorption, the excellent agreement, while encouraging, is not surprising. More complex tests where the adsorption generator is of an arbitrary form are under study. Of course, any adsorption model can replace (m_A/V_A) of Equation (29) to provide a regression equation analogous to (31).

Correction of Burnett Data

The use of several common adsorption models for the correction of adsorption in strictly isothermal Burnett data will now be reviewed. The Langmuir model

$$(m)_i = \frac{f^{(1)}(0) \cdot P_i}{1 + bP_i} \qquad (32)$$

was first applied to the correction of acetone data by Anderson, et al. (1968). Equation (11) provides the shift of the apparent apparatus constant and

$$\frac{P_0}{Z_0} = \frac{P_i}{Z_i} \prod_{k=0}^{i-1} \left[\frac{N + Z_{k+1}K_A\left(\dfrac{1}{1 + b_AP_{k+1}} + \dfrac{S_{R0} - 1}{1 + b_BP_{k+1}}\right)}{1 + Z_kK_A/(1 + b_AP_k)} \right] \qquad (33)$$

in analogy to Equation (13). When $b_A = b_B$,

$$(P_0/Z_0) = (P_i/Z_i) \prod_{k=0}^{i-1} \left[\frac{N + Z_{k+1}K_AS_{R0}/(1 + bP_{k+1})}{1 + Z_kK_A/(1 + bP_k)} \right] \qquad (34)$$

which agrees with Equation (10) of Anderson et al. (1968) although the formulation is different.

Equation (34) can be used to correct Burnett data providing that accurate estimates of the adsorption constants K_A, S_{R0}, and b are possible. With linear adsorption in only one cell, $b = 0$ and S_{R0} is unity (or infinity) so K_A (or K_B)

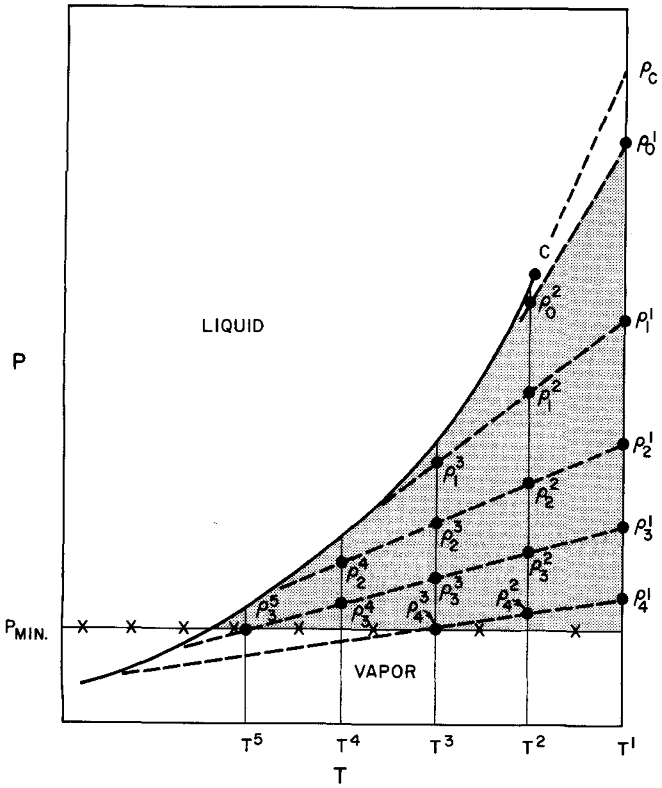

Fig. 6. Pressure-temperature diagram for illustration of Burnett-isochoric method.

may be found from the shift of the apparent volume constant. Otherwise, one or two of the constants must be estimated by approximate methods. All the constants are smooth functions of temperature with K_A and b monotonically decreasing and S_{R0} reasonably constant. Also, K_A is the linear adsorption parameter (low pressure) and b is important only at higher pressures. Figure 5 has shown that linear adsorption can cause an increase in curvature in P_iN^i with decreasing pressure instead of the usual decrease. *For subcritical isotherms, the third virial coefficient of pressure* is generally negative [but not the third virial coefficient of density except for polar gases or for temperatures below $T_R = 0.7$, see Mason and Spurling (1969)] so P_iN^i should be slightly convex upwards at low pressures instead of concave. A good method for estimation of K_A is then to set $b = 0$ and use the criterion that curvature of P_iN^i must decrease smoothly with pressure. Numerical spline methods (Ahlberg et al., 1967) are well suited for this optimization. Recent measurements with cyclohexane (Kerns, 1972) indicate that graphs of $(Z - 1)/P$ versus P at low temperature with $b = 0$ and the optimum K_A show maximum curvature at intermediate pressures instead of smoothly increasing curvature with pressure. The optimum value of b may then be found with the same spline program operating on $(Z - 1)/P$ instead of P_iN^i (or Z).

The BET and potential models, first studied in connection with the Burnett apparatus by Hall (1969), are

$$\text{BET: } (m)_i = f^{(1)}(0) \cdot P_i/(1 - P_i/P_*) \quad [1 + (c - 1)(P_i/P_*)] \qquad (35)$$

and

$$\text{Potential: } (m)_i = \epsilon[\ln (P_*/P_i)]^{-1/8} \qquad (36)$$

Equation (11) provides the shift of the apparent volume constant for the BET model. However, $f^{(1)}(0)$ is infinite for the potential model or $U_0 = S_{R0}$. Equations analogous to (34) and suitable for the correction of Burnett data follow upon substitution of (35) or (36) into the general relation

$$\left(\frac{P_0}{Z_0}\right) = \left(\frac{P_i}{Z_i}\right) \prod_{k=0}^{i=1} \left(\frac{N + Z_{i+1}\alpha_A[(m_A + m_B)_{i+1}/P_{i+1}}{1 + Z_i\alpha_A(m_A)_i/P_i}\right) \qquad (37)$$

CHEMISORPTION

Diagnoses of chemisorption is generally simple as equilibration times of days, weeks, and even longer are common. Chemical analysis of the gas following an extended period in the apparatus will also show the products of reaction. Before initiating Burnett expansions at a given temperature it is wise to attempt a measurement of the vapor pressure with liquid in the cell. A steady increase in pressure for prolonged periods indicates chemisorption. Once a significant amount of the reaction products have formed—whether they exist strictly as a solid coating on the inner cell walls or also in the gas phase—a number of strange occurrences may be observed.

Reaction products in the gas phase produce errors in Burnett data that transcend those caused by simple impurity. First, the reaction equilibrium will generally shift *with pressure. Second, the formation of a product of low* volatility may lead to the unsuspected presence of liquid in the apparatus at pressures below the vapor pressure of the pure reactant.

Solid reaction products are more troublesome, if possible. Experience with ethanol indicates that they cannot be removed entirely by vacuum (Kerns, 1972). An apparatus which had yielded excellent helium calibration data produced erratic results when the calibration was repeated following experiments with ethanol. It appeared that chemisorbed molecules were still coming off the cell walls at low pressures even though the apparatus had been under vacuum for a week following removal of the ethanol. Baking the apparatus at high temperatures while under vacuum speeds the desorption process, but experience with ketones and alcohols indicates that the only satisfactory procedure is to refinish the cell surface. Otherwise, the porous solid residue will greatly enhance physical adsorption. Obviously, both the true volume constant N and the surface-to-volume ratio for physical adsorption are affected by the deposition of nonvolatile solid products of reaction.

In oxygen-containing organic compounds, chemisorption is often the result of catalysis by the chromium and nickel *in the stainless steel of the container. The only prevention,* apparently, is to change the surface by gold plating, glass lining, or vapor coating with a stable polymer.

MOLECULAR ASSOCIATION

The PvT properties of highly polar gases which associate, such as water, alcohols, and ketones, are appropriate for measurement by the Burnett apparatus. Electrical forces of intermolecular interaction often combined with hydrogen bonding to cause strong attraction between molecules which results in relatively high critical temperatures. The vapor pressure of an alcohol may be only 10^4 N/m^2 at 25°C so an apparatus with extremely low pressure capability is required. Unless the apparatus is equipped for high temperature studies ($T > 250°$C), all or nearly all the measurements will be at subcritical temperatures. Equilibration times for molecular association (or dissociation) appear to be rapid and present no problem to the Burnett apparatus. These are the compounds, however, which are most likely to give adsorption problems, both physical and chemical. Otherwise, the only effect of the strong molecular forces of attraction is to lower the compressibility factor and produce highly negative second and third virial coefficients of density. Second virial coefficients for these compounds at 25°C are usually of the order of $-$ 2 m^3/kg-mole or roughly 100 times the positive value of helium. The % accuracy of second virial coefficients of highly polar gases should thus be excellent but is, in fact, about the same as for nonpolar compounds (1 to 5%) due to adsorption, limited pressure range imposed by low vapor pressures and premature truncation of the virial equation. This section will consider primarily Burnett data reduction procedures peculiar to associating gases. The several methods for calculation of association equilibrium constants, fractions of each *n*-mer and entropies and enthalpies of dissociation from virial coefficients are straightforward and available in the literature (Lambert et al., 1949; Woolley, 1953).

First, it is particularly advisable to ground the cell and remove any electrical field sources in the vicinity. All water should be removed from alcohol or ketone samples to prevent unsuspected condensation in the cell. Determination of the vapor pressure curve by the Burnett apparatus prior to PvT data runs is recommended to test purity and chemisorption.

The PvT data should first be analyzed by graphical techniques as the pressure ratio and P_iN^i plots are necessary for diagnoses of physical adsorption. Correction for adsorption should be made on the compressibility factors as noted previously rather than on the virial coefficients. The excellent direct methods such as Hoover et al. (1964) and Hall and Canfield (1967, 1970) must be used with care. Otherwise, adsorption effects may be buried in the digital computer. Truncation of the virial equation must be done with particular caution as the leading coefficients are strongly negative for associating gases at subcritical temperatures and fourth virial contributions, for example, can be important at deceptively low pressure. Extrapolations to zero pressure to obtain U_0, $\lim_{P_i \to 0} P_iN^i$, and the virial coefficients should be done by several methods-graphical, spline program (Kerns, 1972) and standard nonlinear regression programs to obtain a check for consistency. Generally, the curvature in these graphs is considerable for associating compounds. Accurate pressure measurements below 3×10^4 N/m^2 become increasingly important as the temperature decreases. Finally, all adsorption parameters such as U_0 (which should approach N at higher temperatures), $f_A^{(1)}(0)$, b, etc., as well as Z, $(\partial Z/\partial T)_P$, $(\partial Z/\partial P)_T$, and the virial coefficients should each be plotted versus temperature to check for smoothness.

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NOTATION

a, $\bar{b}$ = parameters in the Dieterici equation of state
b = Langmuir adsorption isotherm parameter
B_k = kth virial coefficient of density
B_p = second virial coefficient of pressure
C = BET adsorption isotherm parameter
$f^{(j)}$ = $(\partial^j f/\partial P^j)_T$
J = number of Taylor series terms retained for m
K = number of virial terms retained after truncation
K_A = $\alpha_A f_A^{(1)}(0)$, a positive constant for a Burnett isotherm
m = moles of adsorbed molecules
n = moles of free or unadsorbed molecules
N = $(V_A + V_B)/V_A$, true apparatus constant
P = pressure
P_* = BET and potential model adsorption isotherm parameter
$\bar{P}$ = $(P_{AB} + P_A)/2$
R = gas constant
S_R = surface ratio
T = temperature
U_0 = apparent apparatus constant
v = specific volume
V = volume
W = weighting factor
Z = compressibility factor

Greek Letters

α = (RT/V), a constant
β = $N(1 + K_A)/(N + K_A)$, a constant
γ = $N/(N + K_A)$, a constant
ϵ = potential model adsorption isotherm parameter
ξ = cell distortion correction
ρ = density

Subscripts

A refers to primary volume
B refers to secondary volume
c refers to critical point
i refers to number of isothermal expansions, constant on an isochore
k refers to density virial coefficient number
0 refers to zero pressure

Superscripts

h refers to isotherm
j refers to order of derivative

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Wake Phenomena in a Liquid-Liquid Fluidized Bed

Measurements of the size and rate of shedding of wakes of drops, average drop holdup and velocity of the continuous phase as functions of drop size for kerosene, hexane, and benzene dispersed in water in a liquid-liquid fluidized bed are reported. The average drop size ranged between 3.3 and 4.8 mm. The water velocity was 5.0 to 12.05 cm/s. The average drop holdup was 0.065 to 0.560.

The ratio of wake to drop volume was 0.2 to 2.4, and the rate of wake shedding, reported as time of wake transfer units, was 0.7 to 2.4. At low drop holdups, the effect of single drops and groups of drops is dominant. At high drop holdups, the effect of neighboring drops and wakes is dominant. The wake size is correlated with slip velocity and can be calculated from empirical holdup measurements.

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SCOPE

In extraction equipment and direct contact liquid-liquid heat exchangers, a relative motion exists between a continuous phase and a drop phase. Behind the drops in the direction of the flow of the continuous phase, wakes composed of the continuous phase are attached. In the normal range of flows in such equipment, part of the continuous phase flows through the boundary layers of the drops into the wakes, and elements of the wakes are periodically detached and mix with the continuous phase. All this activity is invisible unless special tracers are used and has until recently been neglected in the correlations of transfer parameters and in the design of such equipment.

Garner and Tayeban (1960) suggested that the flow through the wakes plays a role in mass transfer. Letan and Kehat (1968, 1970), and Kehat and Letan (1971) have shown that the rate of heat and mass transfer in spray columns is determined by wake phenomena. In other types of equipment, such as sieve columns and liquid fluidized beds (in a liquid fluidized bed there is no net flow of the dispersed phase through the column), the wakes of drops also play an important role in the transfer mechanisms.

In order to examine the role of wakes of drops in contacting equipment, information on the drop size and drop holdup distribution, velocity of the phases, size of the wakes of drops and rate of wake shedding, as functions of system properties, dimensions and flow rates is required.

In a recent paper (1971b) we have shown that the data from single drops cannot be used to predict the wake parameters of assemblages of drops. In this study the operational parameters, listed above, were studied experimentally as functions of the flow rate of the continuous phase and average drop size for three organic liquids dispersed in water in a liquid-liquid fluidized bed.

CONCLUSIONS AND SIGNIFICANCE

The average drop size was determined by the nozzle size and the velocity through the nozzle. The local average drop size and holdup increased with height in the fluidized bed. Due to the method of drop formation, the average drop size of any system was independent of drop holdup.

The measured velocity of the continuous phase is higher than the slip velocity, usually calculated by dividing the superficial velocity by the holdup of the continuous phase,

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