Gas Compressibility Factors at High Temperature and High Pressure by the Burnett Method: Methyl Chloride

K. W. SUH and T. S. STORVICK

University of Missouri, Columbia, Missouri

An instrument based on the Burnett method for determining gas compressibility at high temperature and high pressure was constructed. An estimate of the accumulated measurement errors indicate the data should be accurate to eight parts in 10,000. The instrument was calibrated up to 1,000 lb./sq.in. with helium at 200° and 300°C. The average absolute difference between the experimental and the smoothed helium compressibility factor data was 4 and 6 parts/100,000 for the 200° and 300°C. isotherms, respectively. Compressibility factor data for methyl chloride from 200° to 350°C. at 25°C. intervals and at pressures to 5,000 lb./sq.in. are reported. Second virial coefficients for helium and methyl chloride were also obtained.

The Burnett method of measuring gas compressibilities was introduced in 1936 (*1*). Since that time the procedure has been used by several investigators (*2* to *13*) over a wide range of temperatures and pressures. Silberberg, Kobe, and McKetta (*10*) describe an instrument for operation between ambient temperature and 200°C., and Mueller, Leland, and Kobayashi (*6*) describe one for operation at liquid nitrogen temperatures. These instruments are similar to the one described in this work.

The general lack of precision p-v-T measurements at temperatures above 200°C. suggested the need for such an instrument. The Burnett method was selected for this application because its basic simplicity allowed it to be adapted for operation in the range from 150° to 400°C. and pressures between 50 to 5,000 lb./sq.in.

BACKGROUND INFORMATION

The Burnett method of measuring compressibility factors has been described in detail (*6, 10*) and only the important results will be summarized. Only isothermal pressure measurements are required in this method. This is an advantage, since temperature and pressure can be measured with high precision and accuracy, while determination of the system volume and the mass of the sample become more uncertain as the temperature and pressure of the determinations are increased. A fluid such as mercury is not required to confine the test gas, since the volume of the Burnett cell remains constant. This makes it possible to operate the Burnett apparatus at much higher temperatures without introducing the uncertainties of correcting the measured pressure for the vapor pressure of mercury, which is about 31 lb./sq.in.abs. at 400°C. (*14*).

There are disadvantages in using the Burnett apparatus. If the test gas is not easily liquified, it must be vented. If the gas is valuable, it must be collected at low pressure and compressed for reuse, which may introduce impurities. The major disadvantage is the wide spacing of the data points at high pressure and the relatively close spacing at low pressure. This can be overcome by making more than one run, *starting at different initial* pressures; but once the initial pressure is established, the remaining points are determined by the properties of the gas.

BASIC EQUATIONS

The equations for obtaining the instrument constant, the run constant, and the compressibility factors at each expansion have been presented in detail (*6, 10*). The instrument constant N_o is defined as the ratio of the volume of the test cell after an expansion $V_I + V_{II}$ to that before V_I:

$$N_o = \frac{V_I + V_{II}}{V_I} \tag{1}$$

The relationship between N_o, the pressure, and the compressibility factor before and after the j^{th} expansion is

$$\frac{p_{j-1}}{p_j} = N_o \frac{Z_{j-1}}{Z_j} \tag{2}$$

But since

$$\lim_{p_j \to 0} Z = 1 \tag{3}$$

the instrument constant N_o can be determined by plotting (p_{j-1}/p_j) vs. p_j and extrapolating to zero pressure. The precision of this extrapolation can be improved by using a test gas that has a linear isothermal compressibility factor up to reasonably high pressures. Equation (2) further indicates that N_o is temperature dependent.

Equation (2) was developed by assuming that the volumes V_I and V_{II} do not change with pressure. Volume corrections due to elastic deformation as the pressure changes have been estimated (*6*). When V_I and V_{II} are nearly equal and are geometrically similar, this analysis gives the following relation between the instrument constant N_o at any pressure and the constant $N(p_i, p_{i-1})$ at the pressure of the i^{th} expansion.

$$N(p_i, p_{i-1}) = N_o \frac{\left(1 + \dfrac{\Delta V}{V_o}\right)_{p_i}}{\left(1 + \dfrac{\Delta V}{V_o}\right)_{p_{i-1}}} \tag{4}$$

K. W. Suh is at Dow Chemical Company, Midland, Michigan.

The volume corrections ($\Delta V/V_0$ vs. p) were estimated from the Lamè formula by using the procedure described by Mueller (6). This value was relatively unaffected by the temperature in the range 200° to 400°C.

Applying Equations (2) and (4) to the first, second, ... j^{th} expansion and combining the results, we obtain the following relation:

$$p_j = \prod_{i=1}^{j} N(p_i, p_{i-1}) = (p_0/Z_0)\, Z_j \tag{5}$$

The run constant p_0/Z_0 was obtained from Equation (5) by taking the low-pressure limit, Equation (3), to obtain

$$\lim_{p_j \to 0} p_j \prod_{i=1}^{j} N(p_i, p_{i-1}) = p_0/Z_0 \tag{6}$$

The extrapolation of the plot of $p_j \prod_{i=1}^{j} N(p_i, p_{i-1})$ vs. p_j can be done with good precision if sufficient low-pressure points are available in the expansion series.

The compressibility factor of the j^{th} expansion in a run was obtained by using the run constant obtained from Equation (6) and the recursion formula, Equation (5). The accuracy of the Burnett method of determining the compressibility factors is very dependent on the precision with which the run constant p_0/Z_0 and the instrument constant N_0 are determined.

EXPERIMENTAL APPARATUS

There are five basic parts in the experimental apparatus: the expansion cell, vacuum system, charging system, temperature measurement, and the pressure measurement. These will be discussed in turn. A more detailed description is given in reference *15*.

Expansion Cell

The Burnett system consists of two expansion chambers V_I and V_{II} connected by an expansion valve 2 shown schematically in Figure 1. The chambers were 2 in. I.D. by 5 in. long and nearly equal in volume (about 16 cu. in.) The pressure cell was machined from type 304 stainless steel, 4½ in. O.D. by 16 in. long. The upper chamber V_I was welded closed and the lower chamber V_{II} had a compression closure sealed with a 1/16-in. diameter, silver plated, Inconel-X, confined O ring. The O ring was hollow, vented, and had a wall thickness of 0.010 in. The vessel head was prestressed to support twice the internal pressure of the chamber by twelve ½-in. cap screws located in the closure nut that was threaded to the outside of the pressure vessel. Three 1¼-in. type 304 stainless steel cubes were placed in the lower chamber to reduce its effective volume to obtain more evenly spaced data points.

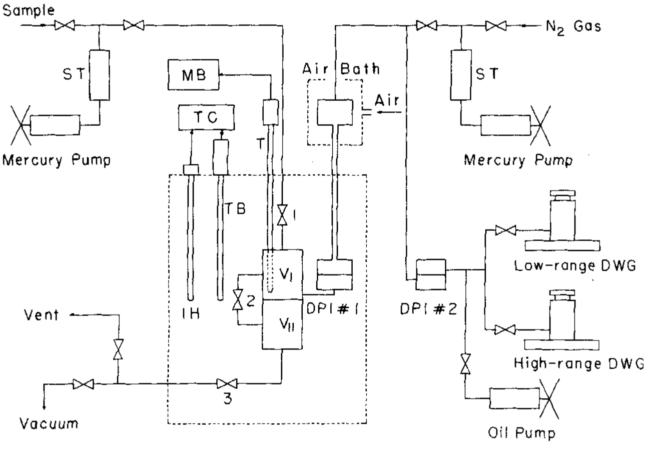

Fig. 1. Schematic diagram of apparatus.

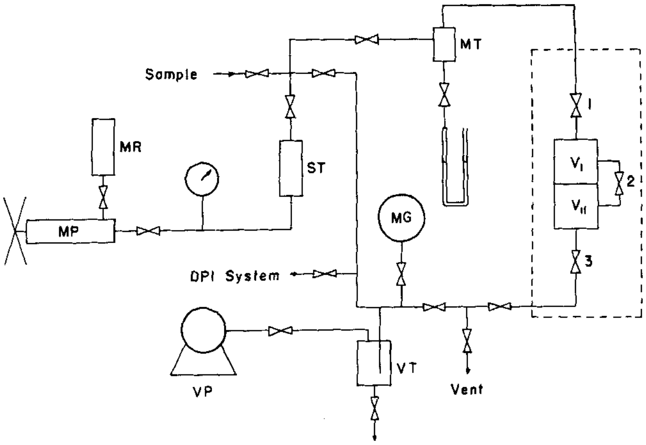

Fig. 2. Schematic diagram of charging and vacuum system.

The charging valve 1 and evacuation valve 3 were commercial 30,000 lb./sq.in. rated, ¼ in., high-pressure valves with extended bonnets, and high-temperature packing. The packing of these valves leaked about 2 std. cu. in. of helium/day at 5,000 lb./sq.in. but effectively sealed under vacuum. This small leak did not interfere with the charging cycle and therefore they could be used as block valves.

The expansion valve 2 required a positive, leakproof seal. A double-seal valve was fabricated from type 304 stainless steel. The lower seal was a fourteen-convolution, 15/32-in. O.D. by 9/32-in. I.D. stainless steel bellows. The valve stem was 14 in. long and sealed with a standard Teflon high-pressure seal outside the constant temperature bath. Gas pressure was applied between the two seals to prevent inelastic deformation of the metal bellows during the gas expansions. The valve functioned satisfactorily up to 5,000 lb./sq.in.

Temperature Measurement

The constant-temperature bath contained fused salt (40% sodium nitrite, 53% potassium nitrate, and 7% sodium nitrate). Manually controlled external heaters served as a heat shield. A general purpose temperature controller (*TC*) (see Figure 1) with a platinum resistance element (*TB*) controlled with on-off switch to the internal heaters (*IH*). The bath temperature could be controlled to ± 0.005°C. of the set point up to 16 hr. when the room temperature was maintained at 25° ± 1.0°C.

A 5/16-in. diameter by 5-in. deep thermowell in the wall of the pressure cell contained a platinum resistance thermometer to measure the test gas temperature. The thermometer coil was located at the midpoint of the upper chamber V_I, the reference level for the pressure measurements. The thermometer was calibrated by the National Bureau of Standards and equipped with a Mueller bridge and optical galvanometer. Although temperature changes of ± 0.001°C. could be readily detected, temperatures were recorded to ± 0.01°C. This uncertainty in the temperature measurement should contribute less than 0.005% error to the measured compressibility factor at 200°C. This error decreases with increasing temperature.

Charging System

The charging system is shown in Figure 2. A 19-cu. in. surge tank (*ST*) was used to inject the test gas into the chamber V_I up to the desired initial pressure. It was made of type 304 stainless steel and designed for 10,000 lb./sq.in. working pressure.

A hand-operated piston pump (*MP*) displaced mercury from a reservoir (*MR*) into the surge tank. A mercury trap (*MT*) prevented mercury from entering the pressure cell. Standard ¼-in., 30,000 lb./sq.in. high-pressure tubing, valves, and fittings were used throughout the system.

Vacuum System

The vacuum system is also shown in Figure 2. A mechanical oil seal vacuum pump (*VP*) rated at 0.1 μ was used to evacuate chamber V_{II} after each expansion. The volumetric displacement of the pump reduced the pressure of V_{II} below 50

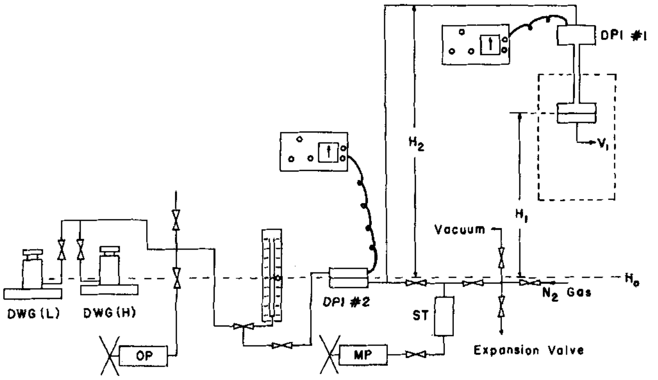

Fig. 3. Pressure measurement.

μ in about 10 min. The pressure on the vacuum system was measured with a McLeod gauge (*MG*). A dry ice trap (*VT*) was located ahead of the vacuum pump to reduce contamination of the vacuum pump oil. The vacuum system was piped with ½-in. I.D. tubing from a point just outside the constant-temperature bath and downstream from the evacuation valve 3 in Figure 2 to reduce the pressure drop in the vacuum system.

Incomplete evacuation of the chamber V_{II} after each expansion contributes an error to the experimental results. If the chamber was evacuated to 50 μ after each expansion, the magnitude of the error would be less than 0.1 p.p.m. for the next expansion. If these errors are additive, the error on the final expansion would be about 1 part/100,000. Care was taken in this work to reduce the pressure below 50 μ between each expansion and it is estimated that the error due to incomplete evacuation should be less than 5 parts/100,000.

Pressure Measurement

The pressure measurement system is shown in Figure 3. Two deadweight gauges (*DWG*) were used to make all the pressure measurements, one with a range from 6 to 2,428 lb./sq.in. and the other from 30 to 12,140 lb./sq.in. A re-entrant type of cylinder with a piston diameter and roundness matched to a tolerance of 5×10^{-6} in. was provided. The resolution of the instruments was about 5 p.p.m. The accuracy was estimated to be 0.01% at 50 lb./sq.in. and increased with increasing pressure.

The oil in the deadweight gauge system was separated from the pressure transmission fluid by a metal diaphragm differential pressure indicator DPI No. 2. This instrument detected a null pressure to ± 0.0003 lb./sq.in.

A high-temperature differential pressure indicator DPI No. 1 separated the pressure transmission fluid from the test gas in chamber V_I. The metal diaphragm of this instrument was located in the constant-temperature bath. A connecting rod from the metal diaphragm extended outside the constant-temperature bath to a second chamber which contained the electronic null position indicator. The null pressure point of this instrument could be detected to ± 0.005 lb./sq.in.

Nitrogen was used as the pressure transmission fluid between DPI No. 1 and No. 2. A hydraulic head correction was made to account for the difference in elevation between the two differential pressure indicators and the temperature gradient on the high-temperature differential pressure indicator.

The barometric pressure was determined to ± 0.003 in. Hg after each expansion. Combining all of the errors in the pressure measurement system gave a probable error of ± 0.02% at 50 lb./sq.in.abs. for the absolute pressure measurements. The error decreases to about ± 0.01% as the pressure is increased to 5,000 lb./sq.in.abs.

ERROR ANALYSIS

In addition to the uncertainties in the measurements, there are other sources of experimental error. The effect of pressure on the instrument constant probably contributes the greatest uncertainty. The fractional change in volume of the pressure cell is estimated to be 0.07% at 5,000 lb./sq.in. and reduces to 0.0006% at 50 lb./sq.in. The uncertainty in the apparatus constant due to this elastic deformation amounts to about 0.001%.

Finally, the use of one instrument constant for all temperatures introduces an uncertainty of about 0.005% in the value of this constant. This error propagates because of the product of this constant occurs in Equation (5). The probable error in the experimental data was estimated to be about 0.05% at the lowest pressures (largest number of expansions) and decreases with each higher pressure in the expansion sequence.

Summarizing the Sources of Error

Source	Estimated error
Temperature measurement	0.005% or less
Evacuation	0.005% or less
Pressure measurement	0.020% or less
Run constant & equipment constant	0.050% or less
Total	0.080% or less

These errors have been estimated on the basis of their contribution to the compressibility factors. This figure represents the probable accuracy of the instrument and probably could be reduced by additional work to obtain better values of the run constant and the instrument constant N_O.

EXPERIMENTAL PROCEDURE

The following sequence of steps was required to make a run: The system was evacuated, the test gas charged to the desired initial pressure in V_I, thermal equilibrium was established, and the expansion series was completed. About 1 hr. was required for each expansion. Thermal equilibrium was established in about 10 min. after an expansion was completed. Each expansion was done slowly to maintain nearly the same pressure on both sides of the metal bellows seal of the expansion valve. The equilibrium pressure was measured with the expansion valve closed so that the instrument constant would not be changed. The expansion valve was opened and closed after an initial reading. A second pressure reading was taken to ensure equilibrium was established.

Before each expansion the volume V_{II} was evacuated to less than 50 μ. The vacuum pump was isolated from the system and the vacuum checked to determine if the expansion valve leaked. Each expansion series was continued until the final pressure was below 100 lb./sq.in.abs., ten expansions were completed, or the pressure was too low to measure accurately on the deadweight gauge system.

Helium Calibration

Helium was selected as the calibration gas because it is known to have a nearly linear isothermal compressibility factor up to 1,000 lb./sq.in. at 200°C. and higher. Four runs were made at 200° and at 300°C.

The instrument constant N_o was obtained by least-squares fitting of p_{j-1}/p_j vs. p_j to a linear equation [see Equation (2)]. Since the absolute error of a pressure measurement is nearly independent of the total pressure up to 1,000 lb./sq.in., the data were weighed in direct proportion to the pressure p_j. The instrument constant was obtained from the $p_j = 0$ intercept and the fitted equation at each temperature. The intercepts are:

$$N_o = 1.599866 \text{ at } 200°\text{C.}$$
$$N_o = 1.599844 \text{ at } 300°\text{C.}$$

An average of $N_o = 1.599855$ was used in all of the compressibility factor determinations. The maximum probable error in this value is estimated to be 3 parts/100,000. Although the data appear to scatter below 60 lb./sq.in. abs., the deviation of helium compressibility factor from linear behavior is so slight that the extrapolation to zero is very precise. The scatter is primarily due to the error in the pressure measurements at the lower pressures.

The smoothed compressibility factor data for helium are reported in Table 1 at 200° and 300°C. The data

TABLE 1. SMOOTHED COMPRESSIBILITY FACTORS FOR HELIUM

p, atm.	200°C.	300°C.
1	1.00028	1.00023
10	1.00282	1.00225
20	1.00564	1.00449
30	1.00844	1.00672
40	1.01124	1.00895
50	1.01402	1.01117
60	1.01680	1.01338
70	1.01957	1.01558
*	0.000037	0.000064
†	0.00030	0.00032
‡	0.0000725	0.0001050

* $|(Z_{exp} - Z_{smooth})|_{ave.}$
† $|(Z_{exp} - Z_{smooth})|_{max.}$
‡ Standard deviation of $(Z_{exp} - Z_{smooth})$.

were smoothed by plotting $(1 - Z)/p$ vs. p for each isotherm on a plot sufficiently large so that the values could be read to 1 part/10,000. The maximum and average deviations of the experimental points from the smoothed data indicate the precision of the data. A low-pressure point on each isotherm yielded the maximum deviation. These two points were more than three standard deviations from the smoothed curve and discarding them would have improved the fit.

The second virial coefficients in the Berlin virial expansion were obtained by extrapolating the $(1 - Z)/p$ vs. p plot to $p = 0$. These results are compared with values obtained from the literature in Table 2 and are in excellent agreement.

The probable error in the second virial coefficients for helium is estimated to be about 0.1 cc./mole and that for methyl chloride approximately 0.2 cc./mole.

Methyl Chloride Data

The compressibility factors for methyl chloride were measured at 200° to 350°C. at 25°C. intervals and up to 5,000 lb./sq.in.abs. At least two series of expansion were made on each isotherm starting at different initial pressures selected to give nearly evenly spaced data points. Large scale plots were used to obtain the run constants p_o/Z_o and the second virial coefficients. The intercepts on these plots could be read with a precision of 0.005%.

The second virial coefficients are reported in Table 3. Hsu and McKetta (*19*) have reported two points that can be compared with this work. The absolute difference between the two coefficients at 200° and 225° are nearly the same.

The smoothed compressibility factor data for methyl chloride are reported in Table 4. The smoothing was done graphically by plotting $(1 - Z)/p$ vs. p and cross plotting $(1 - Z)/p$ vs. T. The data tended to scatter on the 325° and 350°C. isotherms. This may have been due to the initial stages of thermal decomposition of the methyl chloride which occurred at 375°C. The data on the two high-temperature isotherms may be less accurate for this reason. The reported data are accurate to 0.3% or better on all but the 350°C. isotherm, as indicated by the average and maximum deviations of the experimental points from the smoothed data reported in Table 4. The methyl chloride results are less precise than those for helium. The primary source of scatter in the data comes from the extrapolation to zero pressure required to obtain the run constant p_o/Z_o. This scatter could be reduced by using low-pressure (below 100 lb./sq.in.) expansions to account for the slight curvature of the compressibility factor isotherms in this region where the data from the high pressure expansions are least reliable. The Burnett apparatus described here can be used for operation at pressures from 200 lb./sq.in. and down.

Hsu and McKetta (*19*) have reported compressibility factors for methyl chloride at 200° and 225°C. The two sets of smoothed data are shown in Figure 4. The average absolute difference between thirty-two common points of the two sets of data is 0.00072 at 200°C. When the point at 50 atm. is neglected, (this point is more than four stand-

TABLE 2. COMPARISON OF SECOND VIRIAL COEFFICIENTS FOR HELIUM

T, °C.	Source	$-B$, cc./mole
200	This work	10.98
	Silberberg (*10*)	10.77
	Keesom (*16*)	10.10
	Otto (*17*)	11.07
	Schneider (*9*)	11.08
	Wiebe (*18*)	10.71
300	This work	10.59
	Otto (*17*)	10.50
	Schneider (*9*)	10.76

TABLE 3. SECOND VIRIAL COEFFICIENTS FOR METHYL CHLORIDE

	$-B(T)$, cc./mole	
Temperature, °C.	This work	Hsu & McKetta (*19*)
200	144.2	140
225	113.7	119
250	93.62	
275	81.19	
300	68.50	
325	58.71	
350	47.05	

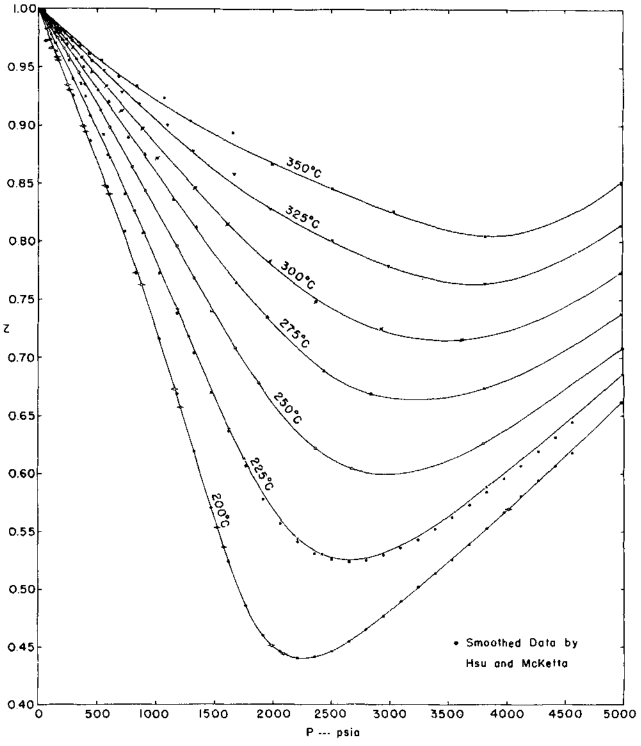

Fig. 4. Compressibility factor of methyl chloride.

Table 4. Smoothed Compressibility Factors for Methyl Chloride

	Z						
P, atm.	200°C.	225°C.	250°C.	275°C.	300°C.	325°C.	350°C.
1	0.9964	0.9971	0.9978	0.9982	0.9985	0.9987	0.9989
5	0.9820	0.9856	0.9888	0.9909	0.9922	0.9935	0.9946
10	0.9637	0.9710	0.9772	0.9814	0.9841	0.9867	0.9887
20	0.9258	0.9408	0.9531	0.9615	0.9673	0.9724	0.9763
40	0.8455	0.8776	0.9020	0.9197	0.9326	0.9425	0.9502
60	0.7592	0.8113	0.8488	0.8770	0.8974	0.9130	0.9250
80	0.6674	0.7427	0.7953	0.8344	0.8632	0.8846	0.9014
100	0.5704	0.6729	0.7430	0.7932	0.8306	0.8580	0.8797
120	0.4858	0.6098	0.6949	0.7555	0.8007	0.8337	0.8598
140	0.4458	0.5609	0.6530	0.7224	0.7741	0.8124	0.8421
160	0.4412	0.5334	0.6224	0.6951	0.7519	0.7943	0.8268
180	0.4544	0.5253	0.6050	0.6764	0.7351	0.7800	0.8146
200	0.4766	0.5313	0.5995	0.6669	0.7236	0.7691	0.8056
220	0.5013	0.5457	0.6028	0.6647	0.7175	0.7622	0.7999
240	0.5266	0.5649	0.6128	0.6674	0.7158	0.7594	0.7977
260	0.5527	0.5879	0.6279	0.6748	0.7186	0.7606	0.7992
280	0.5796	0.6118	0.6465	0.6857	0.7267	0.7667	0.8045
300	0.6074	0.6372	0.6668	0.7006	0.7391	0.7769	0.8140
320	0.6356	0.6626	0.6877	0.7186	0.7551	0.7918	0.8278
340	0.6624	0.6856	0.7077	0.7385	0.7744	0.8109	0.8457
*	0.0024	0.0035	0.0002	0.0017	0.0011	0.0042	0.0072
†	0.0117	0.0142	0.0006	0.0077	0.0062	0.0178	0.0277
‡	0.00366	0.00535	0.00032	0.00276	0.00194	0.00663	0.01150

* $|(Z_{exp} - Z_{smooth})|_{ave.}$
† $|(Z_{exp} - Z_{smooth})|_{max.}$
‡ Standard deviation of $(Z_{exp} - Z_{smooth})$.

ard deviations from the mean difference of all points) this average difference is reduced to 0.0005. From this analysis, the two sets of data agree within the limits of the accuracy of the data.

It is apparent from Figure 4 that the 225° isotherm data differ significantly. Hsu and McKetta indicate that this isotherm may be in error due to mercury vapor present in the Beattie apparatus used to obtain the data. The average absolute difference between these two sets of data is 0.00322, with the Hsu and McKetta data always lower than this work. Since there is nearly a constant difference between the two sets of data at all but the lowest pressures, the error can be assumed systematic and may be due to the mercury vapor.

DISCUSSION

A Burnett instrument has been constructed to make precise and accurate compressibility factor measurements in the range of temperatures from 200° to 350°C. and pressures to 5,000 lb./sq.in. The upper temperature limit of the instrument is restricted by the materials of construction of the instrument and the thermal stability of the test gas. Calibration results on helium at 200° and 300°C. have demonstrated that the compressibility factor measurements can be made with an accuracy of 0.08% or better.

The methyl chloride measurements are claimed to be accurate to 0.3%. This estimated error is based on the average deviation of the smoothed data from the experimental points reported in Table 4. All of the experimental points were included in this average and the reported values should be more accurate than 0.3% for all but the 350°C. isotherm. At 350°C. the methyl chloride may have been thermally decomposing.

ACKNOWLEDGMENT

The authors are grateful for National Science Foundation grant G-24480, which provided funds to construct and operate this instrument. The Office of Research Administration at the University of Missouri provided funds for computational work.

NOTATION

$B(T)$ = second virial coefficient
N_o = instrument constant as defined by Equation (1)
$N(p_i, p_{i-1})$ = instrument constant at p_{i-1} and p_i as defined by Equation (4)
p = pressure
p_j = pressure after j expansions
p_o/Z_o = run constant as defined by Equation (6)
R = gas constant
T = temperature
v = specific volume
V_I = volume of chamber 1
V_{II} = volume of chamber 2
ΔV = change in system volume
Z_j = compressibility factor
$\prod_{i=1}^{j}$ = product of factors from $i = 1$ to $i = j$

LITERATURE CITED

1. Burnett, E. S., *J. Appl. Mech.*, **58**, A136 (1936).
2. Bloomer, O. T., *Inst. Gas. Technol. Res. Bull.*, **13**, 1 (May, 1952).
3. Harper, R. C., Jr., and J. G. Miller, *J. Chem. Phys.*, **27**, 36 (1957).
4. Kramer, G. M., and J. G. Miller, *J. Phys. Chem.*, **61**, 785 (1957).
5. MacCormack, K. E., and W. G. Schneider, *J. Chem. Phys.*, **19**, 845 (1951).
6. Mueller, W. H., T. W. Leland, Jr., and Riki Kobayashi,

A.I.Ch.E. J., 7, 267 (1961).
7. Pfefferle, W. C., J. A. Goff, and J. G. Miller, *J. Chem. Phys.*, **23**, 509 (1955).
8. Schneider, W. G., *Can. J. Res.*, **B27**, 339 (1949).
9. ———, and J. A. H. Duffie, *J. Chem. Phys.*, **17**, 751 (1949).
10. Silberberg, I. H., K. A. Kobe, and J. J. McKetta, *J. Chem. Eng. Data*, **4**, 314, 323 (1959).
11. Watson, G. M., A. B. Stevens, R. B. Evans III, and D. Hodges, Jr., *Ind. Eng. Chem.*, **46**, 362 (1954).
12. Whalley, E., Y. Lupien, and W. G. Schneider, *Can. J. Chem.*, **31**, 722 (1953).
13. Zimmerman, R. H., and S. R. Beitler, *Trans. Am. Soc. Mech. Engrs.*, **74**, 945 (1952).
14. Perry, John, "Chemical Engineers' Handbook," 3 ed., p. 265, McGraw-Hill, New York (1950).
15. Suh, K. W., Ph.D. thesis, Univ. Missouri, Columbia (June, 1965).
16. Keesom, W. H., "Helium," pp. 36-38, Elsevier, Amsterdam (1942).
17. Otto, J., "Handbuch der Experimental Physik," Bd. VIII, Teil 2, 144 (1929).
18. Wiebe, R., V. L. Gaddy, and C. Heins, Jr., *J. Am. Chem. Soc.*, **53**, 1721 (1931).
19. Hsu, C. C., and J. J. McKetta, *J. Chem. Eng. Data*, **9**, 45 (1964).

Manuscript received January 18, 1966; revision received July 14, 1966; paper accepted July 15, 1966. Paper presented at A.I.Ch.E. Dallas meeting.

Partial Control of Linear Inventory Systems

DOUGLASS J. WILDE and URY PASSY

Stanford University, Stanford, California

Feedback and feedforward inventory control systems are derived which give improved probability of holding all inventories between predetermined limits, even when there are fewer controllers than controlled variables. The concept of partial controllability is developed to describe systems with uncontrollable states. An example shows that four tank levels can be held within limits with high probability, with only one manipulated flow rate used.

Sometimes one wishes to regulate a system over which control can be exercised only partially. In a *partially controllable* system, the controlled variables cannot all be driven to their respective set points simultaneously after a disturbance, although they can all be influenced in some way by the manipulated variables. The concept of partial controllability depends on the way the manipulated and controlled variables interact rather than on the nature of the disturbances, be they random or deterministic. Quality of performance of a partially controlled system will, however, depend on the character of the disturbances. A well-designed control scheme gives the best performance possible no matter what sort of external upsets perturb the system, although the quality of this best behavior depends on how badly the disturbances fluctuate.

For example, consider the process in Figure 1. Two substances are delivered, more or less at random, to their respective feed tanks and subsequently pumped to a chemical reactor in constant (say equal) proportions. The reacted mixture is fractionated in a fixed ratio (5 to 1 in this case) into two products which are pumped to separate tanks until ordered by customers who are not entirely predictable. If the flow of mixture through the reactor is manipulated, the levels in all four tanks are influenced. Yet one cannot hold the inventories simultaneously constant at predetermined levels; if one level is fixed, the others must fluctuate uncontrolled. This system is only partially under control.

If the level in only one tank were important, the system would be completely controllable, and a controller could be designed to hold the level constant. Or if the four flows in and out of the tanks did not need to be held in fixed ratios and therefore could be manipulated independently of each other, four controllers could be used to hold each level constant. This system would also be completely controllable. Although powerful design methods can be brought to bear on such completely controllable systems, they do not apply to the partially controllable process of Figure 1. Thus in the present state of technology one finds that such processes are left to the manual regulation of an operator or a manager rather than controlled automatically.

How is it then that an operator can control a partially controllable system when control engineers cannot? The answer is in the interpretation of the word *control*. Control theorists say that a variable is controlled only if it can be driven to some predetermined set point in finite time. Common English usage of the word gives more leeway, however, for the dictionary meaning of the verb *control* is to keep within limits (*4*). Employing the latter definition, an operator does not care what the levels are as long as no tank empties or overflows, and he manipulates the reactor flow to avoid these unsatisfactory circumstances as long as he can. This article shows how to perform such adjustments automatically and, in a certain sense, optimally, even though the system variables are not considered controllable by many control engineers.

Kalman, Ho, and Narendra (*1*), in constructing a rigorous mathematical foundation for control theory, make precisely the distinction needed to resolve this difficulty. They point out that one should not speak of the controllability of systems, but only of the controllability of certain states (or phases) depending on the directly measured controlled variables. Thus the semantic difficulty can be resolved by referring to a variable as *partially controllable* whenever it is the resultant of uncontrollable as well as

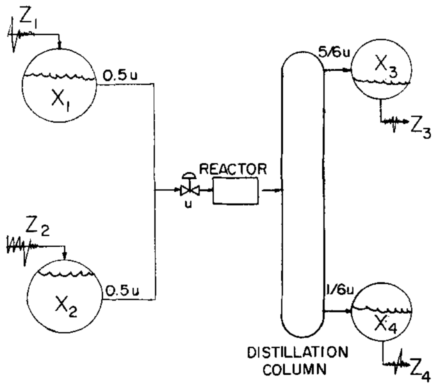

Fig. 1. System flow diagram.