The Compressibility of Carbon Dioxide and Nitrous Oxide at Low Pressures

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A modified Edwards density balance was used to measure compressibility of carbon dioxide and nitrous oxide at pressures under 2.0 atm. and over a temperature range of —30° to 75°C. Second virial coefficients were calculated for the temperatures covered in this investigation and compared with data presented in the literature for both gases. The compressibility data are estimated to be accurate within ±0.10% of the actual compressibility factor.

EXPERIMENTAL APPARATUS

Previous investigators (*9*, *13*, *18*, *22*) have discussed the historical background and principle of operation of the Edwards gas density balance.

Gas adsorption on the surface of the density bulb was a source of error in early compressibility measurements which was eliminated by chrome plating the float and by adding a chrome plated counter balance with the equivalent surface area of the float.

EXPERIMENTAL GASES

The purity and molecular weight of the experimental gases were determined by use of a mass spectrometer. The results are as follows:

Gas	Percent purity	Molecular weight
Argon	99.89	39.931
Carbon dioxide	99.91	43.991
Nitrous oxide	99.92	44.004

EXPERIMENTAL DATA AND RESULTS

The compressibility factors for carbon dioxide and nitrous oxide are presented in Figures 1 and 2, respectively. The experimental data are listed in Table 1.*

The results were fitted to a virial equation of state of the form

$$Z = (PV)/(RT) = 1 + BP + CP^2 + \ldots \qquad (1)$$

The linearity of each isotherm for pressures less than 2.0 atm. allows further simplification to

$$Z = (PV)/(RT) = 1 + BP$$

TABLE 2. SECOND VIRIAL COEFFICIENTS

Temperature, °C.	$-B \times 10^3$ (amt.$^{-1}$)
A. Carbon dioxide	
—30.0	10.03
—15.0	8.19
0.0	6.66
15.0	5.71
30.0	4.85
50.0	3.94
75.0	2.82
B. Nitrous oxide	
—30.0	10.32
—15.0	8.49
0.0	7.07
15.0	5.90
30.0	5.13
50.0	3.94
75.0	2.83

The second virial coefficient *B* was calculated with the present data and Dawson and McKetta's data (*10*) with a least-squares procedure. The values for each isotherm are presented in Table 2. The results from other investigations were compared with the experimental values of this investigation. The virial coefficients of carbon dioxide are in excellent agreement with the work of other investigators especially in the temperature range of 0° to 75°C. These investigators include Maass (*15*), Cawood (*3*, *4*), Schafer (*20*), Batuecas (*1*), MacCormack (*16*), Bottomley (*2*), Cook (*5*), Cooper (*6*, *7*), Pfefferle (*17*), and Cottrell (*8*). The values reported by the earlier investigators deviate less than 5% from the current data. Less than 10% deviation exists in the low temperature range for most points. This corresponds to a difference in compressibility factors of approximately 0.03% at 1 atm. which is less than the estimated accuracy of the present investigation.

There is some inconsistency in the literature data for nitrous oxide. Because of the paucity of consistent literature data a definite conclusion cannot be made in regard to the accuracy of

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* Tabular material has been deposited as document 6626 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

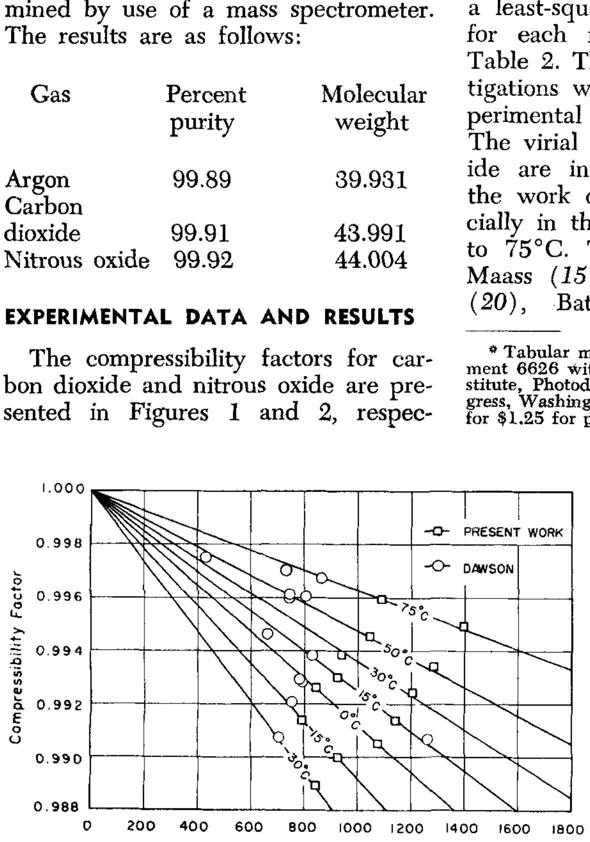

Fig. 1. Compressibility factors for carbon dioxide.

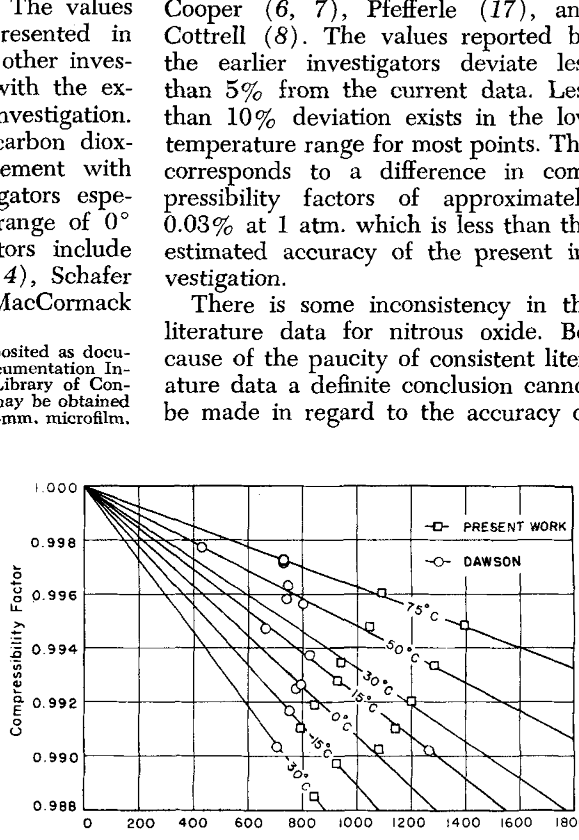

Fig. 2. Compressibility factors for nitrous oxide.

the data as in the case for carbon dioxide. However the excellent agreement with the work of Hirth (*11*), Leduc (*14*), Rayleigh (*19*), and Cawood and Patterson (*4*) substantiates the reliability of this investigation. The values of Bateucas (*1*) and Johnson (*12*) vary considerably from these data.

The actual maximum error of the reported compressibility factors is estimated to be less than ± 0.10%.

ACKNOWLEDGMENT

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Relationship Between Pellet Size and Performance of Catalysts

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The effect of mass transfer resistance in reducing the effectiveness of porous catalysts has been known since the publication of Thiele's classical paper in 1939. The variation in temperature caused by resistance to heat transfer may bring about equally significant changes in effectiveness in some cases. An extension of Thiele's treatment to take exact account of heat transfer resistance leads to a set of nonlinear differential equations that can only be solved numerically.

This paper presents an approximate treatment of the simultaneous effects of resistances to mass and heat transfer. With the limitations imposed by linearizing the equations the formulas derived give the activity and selectivity for any combination of reactions. The use of the results is illustrated by three examples. It is shown that the principal effects are associated with the variation of concentration within the pellet of catalyst and with the difference in temperature between the surface of the pellet and the bulk fluid.

PURPOSE AND SCOPE

The purpose of this paper is to extend the work of Thiele (*10*) on the relation between the size of catalyst pellets and the rate of the catalyzed reaction to take account of two additional effects. Thiele gave a quantitative theory for the diminution in average rate of reaction associated with resistance to diffusion through a porous catalyst, under the assumptions that the temperature is uniform within the pellet and that the composition at the surface of the pellet is the same as the composition in the bulk fluid. There is in addition the tacit assumption that the temperature at the surface of the pellet is the same as the temperature in the bulk fluid. These assumptions are removed from the basis of the present work.

The range of application of the results given below is restricted however by the assumption that the rates of all reactions involved vary linearly with concentrations and with temperature. Although the assumption with regard to concentration is by no means as strong as the assumption that all reactions are of first order, it certainly limits the magnitude of effects that can be described quantitatively. The analogous limitation on the range of temperature that can be covered applies to most reactions because it is rarely that one finds an approximately linear relation between rate and temperature. It must be understood that the ranges of concentration and temperature that are in question here are the ranges covered in the interval between the center of a pellet and the bulk fluid in the immediate neighborhood of that pellet, but not the ranges covered in the whole reactor.

A second restrictive assumption is that the flux of each substance is related to the gradient of its concentration by a constant diffusion coefficient. This assumption is justified if only two substances are present, if all substances present have about the same diffusivity and the reaction does not change the number of molecules, or if the concentrations of all reactants and products are small. A good example of a case in which this assumption is not *justified is* a gas-phase hydrogenation in which hydrogen and the other reactant are fed in comparable concentrations.

In one respect the results given in this paper greatly extend the scope of the theory. There is no limitation in principle on the number of reactions that are going on, or on the number of