Generalized Thermodynamic Properties of Real Gases:

Part I. Generalized PVT Behavior of Real Gases

D. S. VISWANATH and GOUQ-JEN SU
University of Rochester, Rochester, New York

The object of this paper, first in the series dealing with the generalized thermodynamic properties of real gases, is to present generalized compressibility charts in the reduced temperature range of 1.0 to 15.0 and a reduced pressure range of 0 to 40.0. A detailed summary of deviations of the present charts with PVT values of different gases is presented. A summary of the comparison of the present charts with the existing charts is also given.

Generalized compressibility charts represent equations of state for gases in closed form. The generalizations with two parameters is based on the van der Waals theorem of corresponding states or on the modified Su law of corresponding states (*19*). The inherent weakness of the van der Waals theorem of corresponding states is removed in the Su law with the pseudo critical volume $V_{ci} = RT_c/P_c$ instead of the critical volume V_c.

Several compressibility charts (*1, 6, 7, 13*) are available in the literature. Most of the charts are based on the ex-

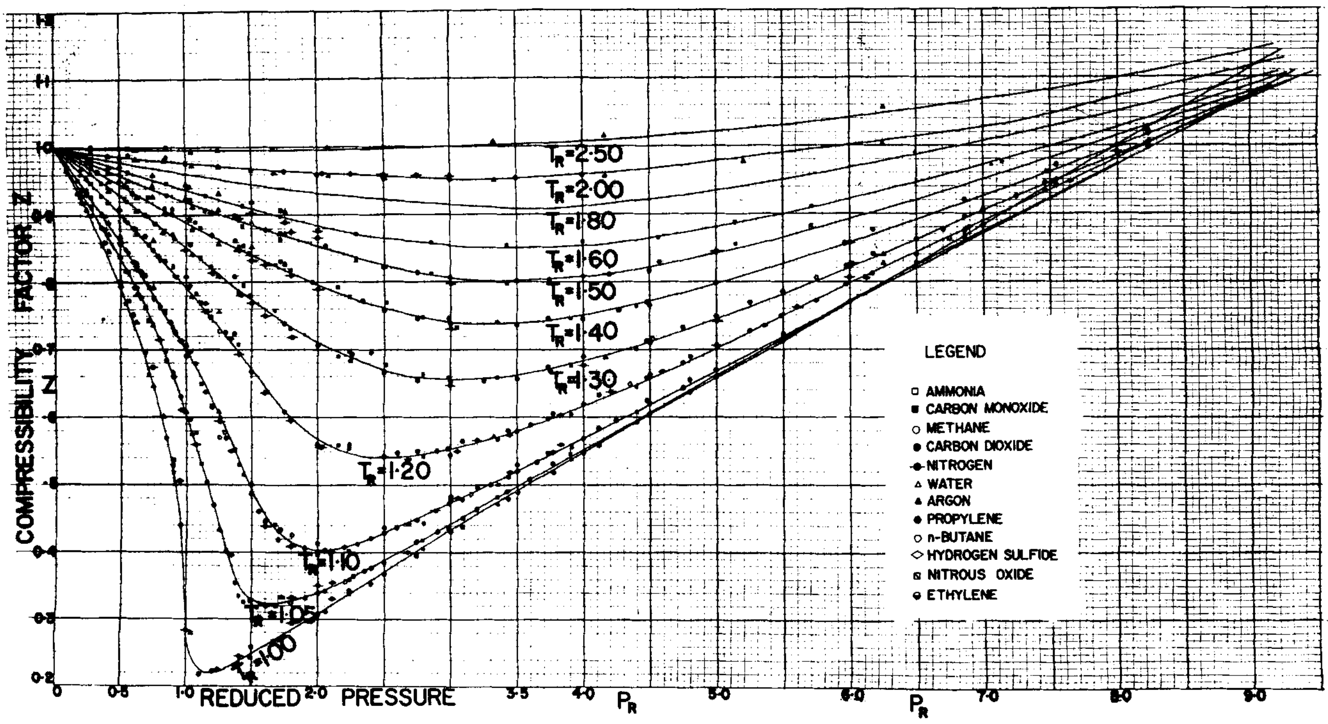

Fig. 1. Generalized compressibility factor chart.

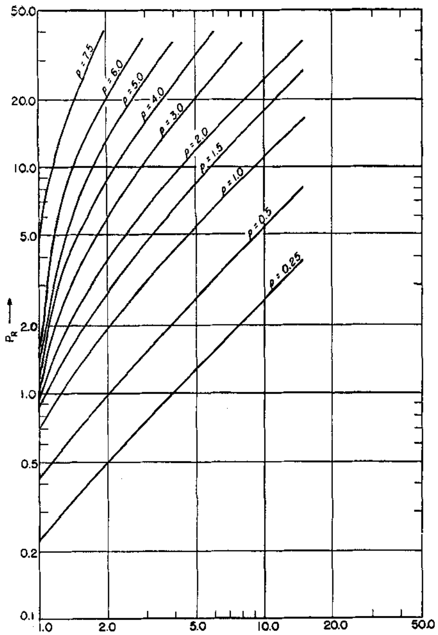

Fig. 2. Generalized isometrics.

perimental PVT data of very few gases. The recent charts are those of Nelson-Obert (*14*), Soparkar (*18*) [based on Su's data (*19*) in the low-pressure region], and Lydersen-Greenkorn-Hougen (*10*). These charts are based on a considerable amount of experimental PVT data of gases. It was found that the charts of Su and co-workers agreed better with the experimental data in certain regions than either Nelson-Obert charts or Lydersen-Greenkorn-Hougen charts (based on $Z_c = 0.27$). But Nelson-Obert charts are in better agreement with experimental data in most of the regions. Thus a necessity to construct more accurate compressibility charts arose, and the work described in this paper accordingly was undertaken.

The compressibility data of Su and co-workers, Nelson-Obert, Lydersen-Greenkorn-Hougen, and data on several gases like *n*-butane, propane, and ammonia constituted the data for the present charts. Apart from the specific references made to the PVT data of gases in Table 3*, most of the data used in the construction of the present compressibility charts are drawn from the references given by Nelson-Obert (*15*). The compressibility charts are constructed by taking average arithmetic, square root, Lorenz values of the data so that the charts will conform to the experimental compressibility values of as many gases as possible. The compressibility factors of several gases at regular intervals of reduced pressure and temperature were tabulated by making plots of actual experimental values against reduced pressure and temperature with reduced temperature and pressure as parameters and reading the compressibility values at regular intervals. The plots made were large enough to enable the compressibility factors to be read to the third decimal place.

Figure 1 shows the conformity of the data for various gases to the present compressibility charts.* Figure 2 shows the generalized isometrics. An extensive comparison of the present charts with those of Su and co-workers, Nelson-Obert, and Lydersen-Greenkorn-Hougen (corresponding to $Z_c = 0.27$) was made, and the deviations are given in Table 1. A summary of the comparison of the present charts with experimental compressibility values of individual gases is given in Table 2. A detailed comparison is given in reference *20*. Experimental compressibility values were compared with the smooth values from these figures, whereas for the comparison with other charts tabular values (*20*) were used.

DISCUSSION

Table 1 shows the deviation for each isotherm and also overall average deviation resulting from the comparison between the values of the present study and those obtained from the charts of Su, Nelson-Obert, and Lydersen-Greenkorn and Hougen. The good conformity of the present values with other charts is not surprising, as they form a part of the data used in the construction of the present compressibility charts.

The compressibility charts were also tested with the experimental Z values for various gases. In the case of hydrocarbons the deviation is about 1%, with the maximum deviations occurring around the critical point. The compressibility chart of Su (*19*) constructed from experimental Z values of seven hydrocarbons also shows a similar deviation. Highly polar gases like ammonia and light gases like hydrogen are difficult to fit the generalized compressibility charts. The present charts show a maximum deviation of about 4.0% and a grand average deviation of

Table 1. Comparison of Present Compressibility Charts with Other Charts

All deviations are percent absolute deviations.
Reduced pressure range covered = 0 to 40.

T_r	Su chart Z_S	Nelson-Obert chart Z_N	Lydersen-Greenkorn-Hougen chart Z_L
1.00	1.117 (25)	1.417	1.927 (30)
1.05	0.505 (9)	1.141	0.695 (30)
1.10	0.571 (9)	1.119	0.694 (30)
1.20	0.620 (25)	0.923	0.698 (30)
1.40	0.439 (25)	0.781	0.789 (30)
1.60	0.526 (35)	0.435	0.444 (30)
1.80	0.659	0.794	0.734 (30)
2.00	0.345	0.471	0.934 (30)
2.20	0.113 (9)	—	—
2.50	0.642	0.904	—
3.00	0.577	—	1.904 (30)
4.00	0.803	0.789	2.240 (30)
5.00	0.502	0.543	—
6.00	0.856	0.992	2.125 (30)
7.00	—	0.652 (9)	—
8.00	0.707	0.251 (10 to 30)	1.663 (30)
10.00	0.263	0.378 (30)	1.369 (30)
15.00	0.189	0.417 (2 to 30)	0.321 (30)
Grand overall average deviation	0.608	0.832	1.260
Total number of points	415	355	339

1. The figures in the parenthesis indicate the maximum reduced pressure other than 40. 2. In this paper the following definitions are used.

Average deviation $= \dfrac{(Z_o - Z_i)/Z_o}{n}$, where $i = S, N, L$, and n is the total number of points.

Grand average deviation $= \dfrac{\Sigma(Z_o - Z_i)}{\Sigma Z_o}$

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* Tabular material has been deposited as document 8056 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $2.50 for photoprints or $1.75 for 35-mm. microfilm.

Table 2. Maximum and Grand Average Absolute Deviation of Present Compressibility Charts with Actual Experimental Values of Individual Gases

Gas	P_r range	T_r range	Grand avg. abs. dev., %	Max. dev., %	No. of points	Source of exptl. data
CH_4	0.25 to 4.50	1.1 to 2.2	1.20	6.0	92	(19)
C_2H_4	0.25 to 4.50	1.0 to 1.6	1.00	10.0	86	(19)
C_2H_6	0.25 to 6.00	1.0 to 1.6	0.70	6.0	79	(19)
C_3H_8	0.25 to 8.00	1.0 to 1.5	1.00	10.0	97	(19)
nC_4H_{10}	0.25 to 8.00	1.0 to 1.3	1.10	18.0	81	(19)
iC_5H_{12}	0.25 to 2.00	1.0 to 1.2	1.90	19.0	26	(19)
nC_7H_{16}	0.25 to 1.80	1.0 to 1.1	2.30	5.0	8	(19)
NH_3	0.09 to 3.60	1.0 to 1.4	0.80	4.0	59	(4)
N_2	0.25 to 1.50	1.0 to 2.2	0.70	4.5	85	(19)
N_2	1.00 to 40.0	1.0 to 1.5	1.50	6.0	91	(2)
H_2	0.08 to 14.0	1.0 to 3.0	4.60	23.0	192	(10)
H_2*	0.05 to 8.40	3.5 to 6.0	1.00	3.0	64	(10)
H_2O	0.25 to 1.75	1.0 to 1.8	1.20	5.7	57	(19)
N_2O	0.28 to 4.40	1.0 to 1.4	0.70	3.7	66	(3)
SO_2	0.26 to 4.05	1.0 to 1.2	2.30	5.0	48	(11)
CO_2	0.69 to 13.7	1.0 to 1.8	1.40	7.0	197	(16)
NO	0.20 to 2.62	1.5 to 2.0	1.30	3.5	32	(9)
CO	0.29 to 28.6	1.5 to 3.5	1.30	3.0	140	(16)
C_3H_6	0.30 to 14.9	1.0 to 1.4	1.30	6.0	84	(8)
A	0.20 to 31.2	1.0 to 4.0	1.40	10.0	220	(5)
H_2S	0.10 to 7.65	1.0 to 1.2	1.70	15.0	70	(17)

* Above Boyle point and with Newton's corrections for critical pressure and critical temperature.

0.8% in the case of ammonia up to a reduced pressure of 3.6, except around the critical region. Nelson and Obert (*15*) in their correlation could not satisfactorily correlate ammonia above a reduced pressure of 1.0. The authors were able however to correlate Z below a P_r of 1.0 with an average deviation of 2.5%, except near the critical region.

Hydrogen correlates very well for T_r up to 3.0 below the critical pressure, the deviation being about 1%. Above the Boyle point (with Newton's corrections for P_c and T_c) the correlation again is within 2% up to a P_r of nearly 14.0. In the region of P_r greater than 1.0 and T_r less than 3.0 the maximum deviation is around 10%, except in the vicinity of the critical point. A major portion even in this region shows a deviation of 5 to 6%, with the deviation decreasing considerably above $T_r = 2.0$. Nelson and Obert (*15*) claim hydrogen to be one of the worst offenders, even in the low-pressure region ($P_r = 0.1$ to 1.0).

Experimental compressibility values drawn from different sources were plotted to obtain data at regular T_r values for a comparison with the present compressibility charts. This avoids any errors due to interpolation between different T_r values on the Z charts. This can, especially around the critical point, lead to serious errors.

The present Z charts are compared with experimental Z values of nineteen gases. This includes highly polar gases (steam, ammonia, hydrogen sulfide, sulfur dioxide), saturated hydrocarbons (methane, ethane, propane, *n*-butane, *i*-pentane, *n*-heptane), unsaturated hydrocarbons (ethylene, propene), low-molecular weight quantum-mechanical gas (hydrogen), average-molecular weight inert gases (nitrogen, argon), and other gases (carbon dioxide, carbon monoxide, nitrous oxide, nitric oxide). The critical compressibility factor, one of the factors leading to a modified law of corresponding states and the one used by Lydersen et al. (*12*) in their study of thermodynamic properties of fluids, varies anywhere from 0.230 for steam to 0.304 for hydrogen for different gases used in the present work.

Sulfur dioxide, nitric oxide, and nitrous oxide lend themselves well for correlation with the present charts. In general polar gases show consistently higher deviations. The data for nitrogen drawn from two different sources correlates very well. The agreement of carbon monoxide ($Z_c = 0.294$) and nitric oxide ($Z_c = 0.256$) with the present generalized charts shows the conformity of compounds with the same molecular structure having different critical compressibility factor. The same can be said about water ($Z_c = 0.230$) and hydrogen sulfide ($Z_c = 0.284$).

NOTATION

P_r = reduced pressure = P/P_c
T_r = reduced temperature = T/T_c
V_r = reduced volume = V/V_c
V_{ci} = pseudo critical volume = RT_c/P_c
Z = compressibility factor = PV/RT
Z_o = compressibility factor from present charts
Z_H = compressibility factor from reference *10*
Z_N = compressibility factor from reference *14*
Z_S = compressibility factor from references *18* and *19*
ρ = pseudo reduced density = V_{ci}/V
subscript *c* refers to the property at the critical point

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