Laws of Corresponding States

L. NELSON and E. F. OBERT
Northwestern Technological Institute, Evanston, Illinois

Various laws of corresponding states are examined briefly in this paper to show the corrections that are in common use to increase the accuracy of forecasting compressibility factors. Two trends are noticeable: (1) the use of specific compressibility charts with the results generalized for all gases either by corrections related to z_c (the compressibility factor at the critical point) or by the use of pseudocritical properties and (2) the use of a true generalized chart based upon averaged data. It is shown that the selection of the plot parameters affects the accuracy of the generalized chart. In recent years reduced parameters based upon kinetic theory have been proposed but for a restricted class of gases (nonpolar gases with spherically symmetrical molecules and negligible quantum effects). It is shown that the kinetic parameters are directly related to the critical constants and also that the kinetic parameter charts can be used for all gases without serious loss of accuracy.

The compressibility factor z is defined:

$$z = \frac{pv}{RT} \tag{1}$$

In terms of reduced properties relative to the critical constants, Equation (1) is equivalent to

$$z = \frac{p_r v_r}{T_r} z_c \tag{2}$$

where z_c is the compressibility factor at the critical point. A compressibility chart can be constructed to correlate z with two selected reduced properties, such as T_r and p_r, with acceptable accuracy for most gases. As an approximation therefore

$$z = f\,(T_r,\ p_r)_{\mathit{all\ gases}} \tag{3}$$

The implications of Equation (3) and other laws of corresponding states have been discussed many times [(*1* and *2*) for examples], but several aspects of the generalized laws are not usually recognized. It may be considered that for any one gas, as z is a state property, an exact functional relationship exists between z and any two of the independent properties p, v, and T. If p and T are selected so that for several gases $T_{ra} = T_{rb} = T_{ri}$ and $p_{ra} = p_{rb} = p_{ri}$, then by Equation (2), which is also an exact equation,

$$\frac{z_a}{z_b} = \frac{v_{ra}}{v_{rb}} \, \frac{z_{ca}}{z_{cb}} \tag{4}$$

Equation (4) shows that the generalization of Equation (3) is successful for gases having essentially the same z_c values because the van der Waals law of corresponding states,

$$v_r = f\,(T_r,\ p_r) \tag{5}$$

holds with adequate precision; the generalization is successful for gases having different (or the same) z_c values because the modified law of corresponding states proposed by Su(*3*),

$$v_r' = v_r z_c = f\,(T_r,\ p_r) \tag{6}$$

holds with adequate precision. It is emphasized that where z_c values are essentially constant, the regions of the generalized chart where correlation is exceptional can be found only by trial. Similarly, when gases have different z_c values, obviously from Equation (2) correlation at or near the critical point will be poor, but this is no assurance that correlation will continue to be poor in regions other than the critical. In other words a compensating effect for z_c is the failure of Equation (5) to hold exactly for all gases. Thus gases with the same z_c value usually correlate closely on the chart, but this happens because the molecular structures are closely related. When the structures or molecular laws of force are different, gases will not correlate well no matter whether the z_c values are equal or not (and an additional parameter becomes necessary: a quantum parameter for the light gases such as helium and hydrogen; a dipole-moment parameter for polar gases, such as the freons, water, and ammonia; and size or shape parameters for the complex organic gases).

z_c CORRECTION FACTORS

Meissner and Seferian (*2*) have published correction charts to account for deviations in z_c between gases. These charts are useful when z values below 0.6 are indicated and *when the molecular structures are closely related.* The law of corresponding states for their work has the form

$$z = f\,(T_r,\ p_r,\ z_c) \qquad (7)$$

The corrections can be ignored however for regions above $T_r = 1.3$ and also for all similar gases with values of z_c between 0.25 and 0.28. In the latter case a difference of over 10% exists in z_c; yet correlation on the compressibility chart is well within 2 1/2% for most gases.

A fundamentally correct method for modifying the generalized z values to account for the deviations of polar gases has been recently proposed by Hall and Ibele(*13*). Their work is based upon a law of corresponding states of the form

$$z = f\,(T_r,\ v_r',\ \mu_r) \qquad (7b)$$

where μ_r is a reduced dipole moment. The corrections of Hall and Ibele enable z values for the polar gases to be obtained with surprising accuracy from a generalized compressibility chart (such as Figure 1). However, the important by-product of their work is the added reliance that can now be given to generalized property charts when allowances are made for the type of molecular structure.

CHANGE IN INDEPENDENT VARIABLE

The inconsistency between Equations (2) and (5) was first recognized by Onnes(*4*), who proposed combining z_c and v_r because in those days critical volumes were open to serious question. The Onnes transformation yields the Su law of corresponding states, Equation (6), which is equivalent to Equation (3), as

$$v_{r'} = z\frac{T_r}{p_r} = \frac{v}{RT_c/p_c} \qquad (8)$$

For that matter, the variable z_c could have been combined with either T_r or p_r, rather than v_r, to yield a pseudoreduced temperature and a pseudoreduced pressure:

$$p_{r'} = \frac{p}{RT_c/v_c} \qquad T_{r'} = \frac{T}{p_c v_c/R} \qquad (9)$$

The laws of corresponding states for these two cases are of the form

$$f\,(z,\ T_r,\ v_r) = 0 \qquad (10)$$

$$f\,(z,\ p_r,\ v_r) = 0 \qquad (11)$$

The correlations implied by Equations (3), (10), and (11) are not equivalent because none of the "laws" are exactly true. No one to the authors' knowledge has investigated which of the three equations would best serve for a generalized compressibility chart, probably because the critical volume has in the past been either unknown or else a variable of some disrepute. For this reason a study was made of twelve gases (CH_4, C_2H_4, N_2, NH_3, H_2, CO_2, CO, Ne, C_3H_8, Xe, A, and air), which indicated that a chart based upon one equation would yield regions of improved correlation relative to charts based upon the other two equations, and of course the opposite trend was also true for other regions. For one example the following data for water ($z_c = 0.232$) and methane ($z_c = 0.289$) at reduced pressures less than $p_r = 1.5$ may be considered:

MAXIMUM DEVIATIONS IN z_{exp}

Chart of	$T_r = 1.1$	$T_r = 1.3$	$T_r = 1.8$
$z = f(T_r, p_r)$	0.05	0.038	0.015
$z = f(T_r, p_{r'})$	0.06	0.015	0.004

Thus for these two gases correlation has been improved in the higher T_r regions with some loss of accuracy near the critical. It is suggested that further work along this line may prove profitable.

EMPIRICAL PSEUDOCRITICAL CONSTANTS

To improve the correlation of data, corrections can be applied to the critical constants. Such corrections can be found by either graphical or analytical methods but in both methods a solution by trial is required. Empirical corrections have been proposed by Morgan and Childs(*5*) and by Maslan and Littman(*6*), among others. A study of certain of these corrections shows that the correction does no more than to shift the region of deviation, and unsuspected errors may arise; for example, the so-called Newton corrections for H_2 and He ($T_c + 8$, $p_c + 8$) when used in regions below the Boyle-point isotherm have been reported by several investigators(*2, 7*) to cause errors as much as 40% in z although improving considerably the correlation at higher temperatures. It seems reasonable to conclude that the selection of correction factors by trial, because of the labor involved, is practically an impossibility.

THEORETICAL PSEUDOCRITICAL CONSTANTS

A means for obtaining the variable correction factors for a selected group of fluids without undue labor is now available by a method derived from statistical mechanics theory. Hirschfelder, Bird, and Spotz(*8, 9*) have developed a virial equation of state based upon the Lennard-Jones force potential. Their work is limited however to the semisymmetrical nonpolar gases, and the analytical results include only the effects of the first three virial coefficients. From the underlying theory, reduced quantities, first proposed by deBoer(*10*), can be defined:

Reduced density

$$\rho_{r'} = b_o\rho \qquad (12)$$

Reduced temperature

$$\tau = \frac{T}{\epsilon/k} \qquad (13)$$

Reduced pressure

$$p_{r'} = \frac{p}{R\,(\epsilon/kb_o)} \qquad (14)$$

The kinetic constants b_o and ϵ (and the gas constants k and R) will not be discussed here since several papers on them are available in the literature (*10, 11, 12*). The important point is that this analytical work rests upon a law of corresponding states of the form

$$f\,(\rho_{r'},\ \tau,\ p_{r'}) = 0 \qquad (15)$$

which is equivalent, for one example, to

$$f\,(z,\ \tau,\ p_{r'}) = 0 \qquad (16)$$

The Hirschfelder-Bird-Spotz tables (*9*) are limited to the low-density region (up to 40% of the critical density) since evaluations of the fourth and higher virials were not made. But if values of the reduced parameters are plotted as in Figure 1 from experimental data [details of construction in (*7*)], the resulting plot represents a virial equation with an infinite number of terms*. In other words, Figure 1 extends by graphical means the Hirschfelder-Bird-Spotz tables to regions of high density.

Once the kinetic parameters are determined, pseudocritical constants can be directly calculated from the following equations and Equations (12), (13), and (14):

---

*A series of various compressibility charts can be obtained by writing to the authors.

$$\tau = \frac{T}{C_1 T_c} \qquad (17)$$

$$p_r' = \frac{p}{C_2 p_c} \qquad (18)$$

$$\rho_r' = \frac{\rho}{C_3\ \rho_c} \qquad (19)$$

with values for various gases as shown in Table 1.

Example 1. Find the compressibility factor for methane at 251.5°K. and 131.3 atm.

Solution

From Table 1,

$$\tau = \frac{T}{C_1 T_c} = \frac{251.5}{0.775\ (191)} = 1.70$$

$$Rp_r' = \frac{Rp}{C_2 p_c} = \frac{82.06\ (131.3)}{3.79\ (45.8)} = 62.1$$

$$\left(\text{Note } R = 82.06 \frac{\text{cc. atm}}{\text{mole °K}}\right)$$

From Figure 1, $z = 0.66$ ($z_{exp} = 0.659$)

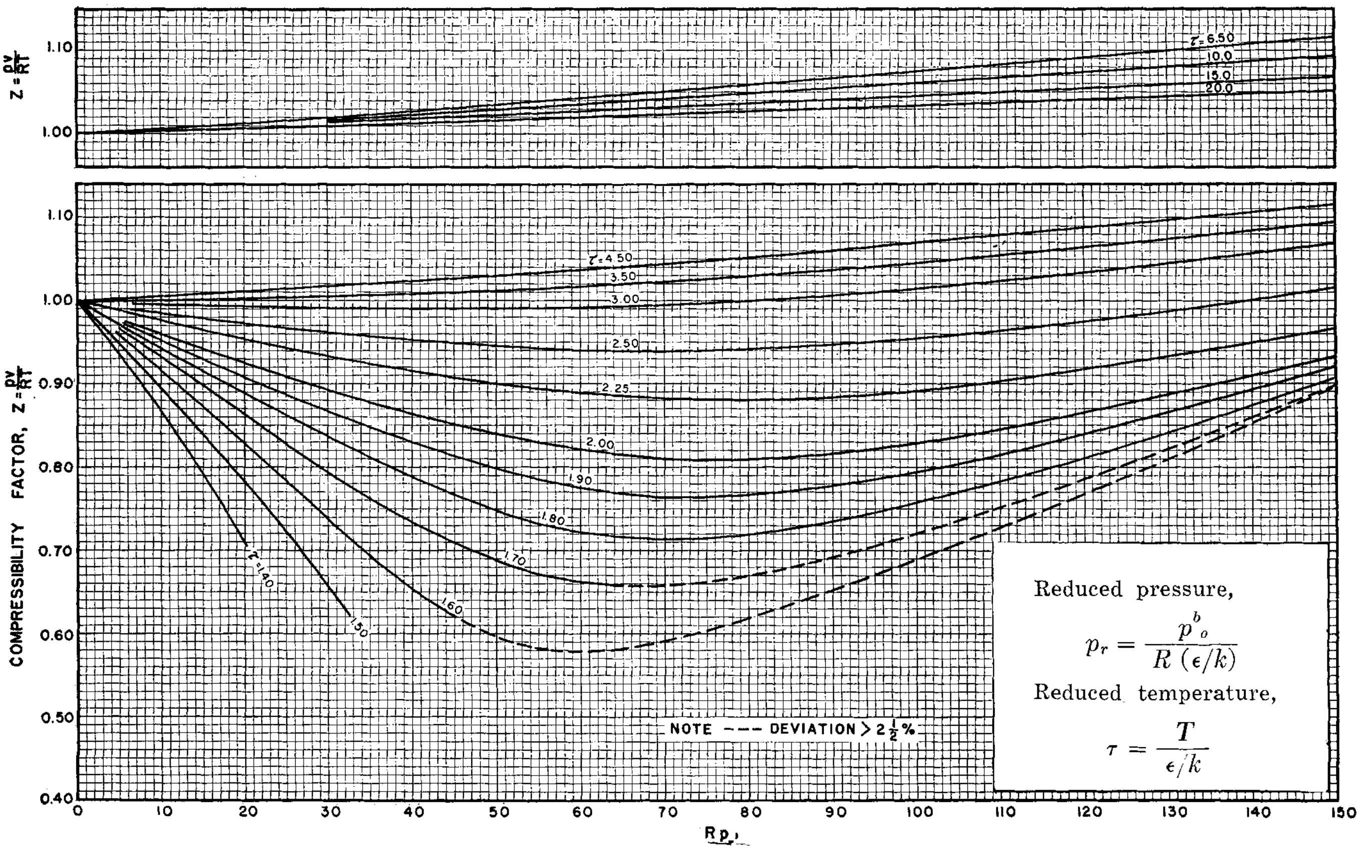

Fig. 1. Generalized Compressibility Chart.

Table 2 has been constructed to show the agreement of the chart with experimental data and with values obtained from existing charts. The data were selected not for high z values, but to agree essentially with Table 2 of Maslan and Littman(*6*). Figure 1 does not include the critical region [where the method and corrections of Meissner and Seferian(*2*) may be preferable].

As an aside comment on the use of Figure 1, it should be noted that the isotherms for nitrogen correlate other gases either on a chart based on critical constants or on a chart such as Figure 1. This fact allows the Bird-Spotz tables and Figure 1 to be extended to include all gases with a fair degree of accuracy (at z values above .6). Equations (12), (13), and (14) can be generalized by substituting reduced and critical values of nitrogen for ρ, T and p, for example,

$$\tau = \frac{T}{\epsilon/k} = \frac{T_r T_{c\mathrm{N}_2}}{(\epsilon/k)_{\mathrm{N}_2}} =$$

$$T_r\left[\frac{126.3}{95.4}\right] = 1.325\ T_r \qquad (20)$$

$$Rp_r' = \frac{p}{(\epsilon/k\ b_o)} = \frac{p_r\ p_{c_{\mathrm{N}_2}}\ b_o}{\epsilon/k} =$$

$$p_r\left[\frac{33.5\ (64.1)}{95.4}\right] = 22.52\ p_r \qquad (21)$$

In the same manner, pseudoforce constants can be determined:

$$\epsilon'/k = 0.756\ T_c \qquad (22)$$

$$b_o' = 17\frac{T_c}{p_c} \qquad (23)$$

Example 2. Find the compressibility factor for ethylene at 425°K. and 126 atm.

Solution

$$p_r = \frac{p}{p_c} = \frac{126}{50.5} = 2.5$$

$$T_r = \frac{T}{T_c} = \frac{425}{283.1} = 1.5$$

With Equations (20) and 21),

$$\tau = 1.325\ T_r = 1.325\ (1.5) = 1.99$$

$$Rp_r' = 22.52 p_r = 22.52\quad (2.5) = 56.3$$

Figure 1 for these values yields

$$z = 0.822$$

which is also the experimental value.

TABLE 1.—A COMPARISON OF THE CRITICAL CONSTANTS AND THE KINETIC CONSTANTS FOR SOME SEMISPHERICAL NONPOLAR GASES

Substance	T_c°K.	p_c atm.	v_c cc./mole	ϵ/k °K.	b_0 cc./mole	C_1	C_2	C_3
N_2	126.3	33.3	79.8	95.4	64.1	0.752	3.65	1.24
O_2	154.8	50.1	74.4	117.0	54.4	0.758	3.53	1.36
Air	132.5	37.2	82.9	102.0	60.3	0.769	3.73	1.33
Ne	44.4	26.9	41.7	34.9	27.1	0.788	3.94	1.54
CO	132.9	34.5	90.0	100.2	67.2	0.752	3.55	1.34
CH_4	191.0	45.8	98.7	148.2	70.2	0.775	3.79	1.41
A	150.7	48.0	75.2	119.8	49.8	0.794	4.29	1.51
Xe	289.8	57.9	113.7	221	86.9	0.764	3.60	1.31
Kr	209.4	54.2	107.3	117	58.9	0.820	4.38	1.83
H_2	33.2	12.8	65.0	29.2	29.8	0.877	6.25	2.18
				Average (except H_2)		0.770	3.82	1.43

TABLE 2.—COMPARISON OF EXPERIMENTAL DATA FOR SOME NONPOLAR GASES WITH THE GENERALIZED COMPRESSIBILITY CHARTS

	Temp. °K.	Pressure atm.	Exp., z	Maslan & Littman Chart z	Morgan & Childs Chart z	Nelson & Obert Chart z
Neon	60.04	59.77	0.712	0.730	0.680	0.715
	90.5	41.37	0.964	0.950	0.950	0.967
	293.1	61.7	1.040	1.030	1.020	1.043
Argon	157.26	41.9	0.673	0.700	0.675	0.705
	215.4	35.1	0.925	0.917	0.920	0.921
	293.5	61.7	0.970	0.956	0.962	0.964
	373.2	188.0	1.015	0.980	1.020	1.006
CO	273.2	150	0.989	......	0.962	0.987
	323.2	200	1.061	......	1.054	1.064
	473.2	200	1.101	......	1.095	1.103
CH_4	248.2	200	0.697	......	0.710	0.700
	323.2	200	0.881	......	0.900	0.874
	473.2	300	1.070	......	1.085	1.073

If the Bird-Spotz tables are to be used, Equations (22) and (23) will yield the correct pseudoconstants for the Bird-Spotz equations. If the real-force constants listed by Bird-Spotz for ethylene were to be used, the z value would be greatly in error as ethylene does not have the spherical symmetry of the gases listed in Table 1.

It should be emphasized however that the method shown in Example 2 can yield no better results than a good compressibility chart based upon critical constants. The advantage of the proposed method lies in the derivatives of the Bird-Spotz tables, which allow thermodynamic properties to be readily calculated (rather than to find compressibility factors). Since the computations for property values are tedious, no example is given here; the foregoing discussion and Equations (20) to (23) outline sufficiently the proposed method.

NOTATION

b_o = kinetic constant = $2/3\pi N r_o^3$

b_o' = pseudokinetic constant = $17\ T_c/p_c$

C_1 = kinetic critical-temperature constant = $\dfrac{\varepsilon/k}{T_c}$

C_2 = kinetic critical-pressure constant = $\dfrac{R(\varepsilon/k)}{b_o p_c}$

C_3 = kinetic critical-density constant = b_o/ρ_c

k = Boltzmann constant

N = Avogadro's number

p = pressure, atm.

p_c = critical pressure

p_r = reduced pressure = p/p_c

p_r' = pseudoreduced pressure = $p\ v_c/RT_c$ also, kinetic reduced pressure = $p\ k\ b_o/R\varepsilon = p/c_2 p_c$

R = universal gas constant = 82.06 cc.atm./mole °K.

r_o = collision diameter between two molecules with negligible kinetic energy

T = absolute temperature, °K.

T_c = critical temperature

T_r = reduced temperature = T/T_c

T_r' = pseudoreduced temperature = $RT/p_c v_c$

v = specific volume = cc./mole

v_c = critical volume

v_r = reduced volume = v/v_c

v_r' = pseudoreduced volume = $p_c v/RT_c$

z = compressibility factor = pv/RT

z_c = compressibility factor at the critical point = $p_c v_c/RT_c$

Greek Letters

ε = kinetic force constant or maximum energy of attraction between two molecules

ε' = pseudoforce constant = $0.756\ T_c k$

$\rho_{r'}$ = kinetic reduced density = ρb_o

τ = kinetic reduced temperature = $T\ k/\varepsilon = T/C_1 T_c$

μ = molecular dipole moment

μ_r = reduced dipole moment = $\mu^2/(RT_c)\ (v_c/N)$

LITERATURE CITED

1. Joffe, J., *Chem. Eng. Progr.*, **45**, 160 (1949).
2. Meissner, H. P., and R. Seferian, *Chem. Eng. Progr.*, **47**, 579 (1951).
3. Su, G. J., *Ind. Eng. Chem.*, **38**, 803 (1946).
4. Kammerlingh Onnes, H., *Commun. Phys. Lab. Univ. Leiden*, **11**, *Suppl.* 23, 115 (1912).
5. Morgan, R. A., and J. H. Childs, *Ind. Eng. Chem.*, **37**, 669 (1945).
6. Maslan, F. D., and T. M. Littman, *Ind. Eng. Chem.*, **45**, 1566 (1953).
7. Nelson, L. C., and E. F. Obert, *Trans. Am. Soc. Mech. Engrs.*, **76**, 1057 (October, 1954).
8. Hirschfelder, J. O., R. B. Bird, and E. L. Spotz, *Trans. Am. Soc. Mech. Engrs.*, **71**, 921 (1949).
9. Bird, R. B., and E. L. Spotz, *Univ. Wisconsin, CM*-599 (May, 1950).
10. DeBoer, J., and A. Michaels, *Physica*, **6**, 97 (1939).
11. Hirschfelder, J. O., R. B. Bird, and E. L. Spotz, *Chem. Revs.*, **44**, 205 (1949).
12. Lennard-Jones, J. E., *Proc. Roy. Soc. (London)*, **A106**, 463 (1924).
13. Hall, N. A., and W. Ibele, Preprint Paper 54-A-140, Am. Soc. Mech. Engrs. (Dec. 3, 1954).