

Modified Law of Corresponding States for Gases

OSCAR T. BLOOMER and RALPH E. PECK

Institute of Gas Technology, Chicago, Illinois

A new correlation is presented for predicting the pressure-volume temperature relations of nonpolar (and slightly polar) gases. The correlation modifies the law of corresponding states in which a third parameter, the slope of the pseudocritical isometric in dimensionless form, is introduced. This parameter is introduced in a simple manner by multiplying the reduced pressure and temperature of the gas by a factor which can be easily calculated or read from a graph. This gives the corrected reduced pressure and temperature which can then be used with a generalized compressibility factor chart in place of the true values. The correlation is accurate for densities up to about 1.2 times the critical density.

A detailed comparison of the method with data on twelve pure gases showed that by introducing this parameter into the law of corresponding states the average error was decreased from 1.598 to 0.320%. The parameter S can readily be determined from experimental PVT data, and only one isotherm is required. S is related to the vapor-pressure curve for a substance as characterized by the critical pressure and the ratio of the critical temperature to the normal boiling temperature, and a simple method is proposed for predicting S when no experimental data are available.

A new set of generalized compressibility factor and fugacity to pressure ratio charts is presented for use with the proposed correlation. A method is also presented for determining the thermodynamics functions.

The basis for the correlation presented in this paper is two well-known properties of gases. The first is the linearity of the isometrics (lines of constant density) when plotted on a P - T diagram. At densities below the critical density the isometric curves slightly downwards toward the T axis (negative curvature). As the critical density is approached, the curvature becomes less until in the vicinity of the critical density the isometrics are almost exactly linear over a considerable temperature range.

The second property concerns the critical isotherm. When the critical isotherm of various gases is plotted on a plot of the compressibility factor vs. the reduced pressure, many gases will plot along the same line to a surprising degree of accuracy. This is by no means true for other isotherms either above or below $T_r = 1.0$.

It has been shown by Cope, Lewis, and Weber (3) that the modification to the law of corresponding states which results when the compressibility factor is plotted as a function of the reduced pressure and reduced temperature requires that the reduced density (d/dc) be replaced by the pseudoreduced density (d/d'_c), where

$$d'_c = \frac{P_c}{RT_c Z'_c} \quad (1)$$

Z'_c was arbitrarily given the value of 1.0 by Su (7) but will be given the value of 0.29 in this paper to make it correspond closely in value to the true critical density of many nonpolar gases.

Since the pseudocritical density is almost exactly linear for a pure gas,

its equation may be written as

$$P = I + sT \quad (2)$$

where

$$s = (\partial P / \partial T)_{d'_c}$$

When one writes Equation (2) in reduced form

$$P_r = I/P_c + (s T_c / P_c) T_r \quad (3)$$

When $T_r = 1.0$, $P_r = 1.0^*$, and

$$I/P_c = 1 - s T_c / P_c \quad (4)$$

Substituting (4) into Equation (3) one gets

$$P/P_c = 1 - (s T_c / P_c) + (s T_c / P_c) T_r / T_c \quad (5)$$

Now

$$Z = P / RT d'_c$$

Substituting into this equation the value of P obtained from Equation (5) one gets

$$Z = (P_c / RT_c d'_c) (T_c / T) - (s / R d'_c) (T_c / T) + (s / R d'_c) \quad (6)$$

and finally

$$Z = 1/T_r (Z'_c - S) + S \quad (7)$$

where

$$S = s / R d'_c \quad (8)$$

If the law of corresponding states were valid for all substances, then S would be a universal constant for all substances.

One should consider the requirements necessary to have the compressibility factors for two different gases

* This is not strictly true for the pseudocritical isometric. (It is true for the critical isometric.) The error is however negligibly small because at the critical temperature the pressure is equal to the critical pressure to within a fraction of a percentage over a wide range of densities (from a reduced density of about 0.8 to about 1.30).

equal along the pseudocritical isometric. This is obtained at once from Equation (7).

$$Z_1 = 1/T_{r1} (Z'_c - S_1) + S_1 = Z_2 =$$

$$1/T_{r2} (Z'_c - S_2) + S_2 \quad (9)$$

If there is available a compressibility-factor chart for substance one, then the above equation can be solved for T_{r1} which is the reduced temperature line on the chart for substance one which will have the same value of the compressibility factor that substance two has at T_{r2} . This equation then provides a method of using for any substance a compressibility-factor chart based on the data for a reference substance. Aside from the critical pressure and temperature it requires only that the slope of the pseudocritical isometric be known. This method will certainly be valid for the pseudocritical isometric.

It is now assumed that the above transformation equation is valid for all constant pseudoreduced density lines $d'_c = d/d'_c$, not just for the $d'_c = 1.0$ line. The justification for this assumption must rest on a detailed comparison with experimental data. It is immediately evident however that it is a very good approximation for the critical isotherm, since the above equation gives $T_{r1} = 1.0$ when $T_{r2} = 1.0$, and as previously pointed out the critical isotherms of different gases do indeed very nearly coincide, at least up to a reduced pressure of 1.0 (pseudoreduced density of 1.0). This fact furnishes a hint that this equation will probably be valid for all constant reduced density lines at least up to $d'_c = 1.0$. The detailed comparison of the method with experimental data on twelve pure gases is presented in a following section. It suffices for the present to state that the equation is very satisfactory for pseudoreduced densities up to about 1.2 but that above this serious errors may be introduced.

Since in engineering practice the pressure and not the density is usually known, it is necessary to develop an equation corresponding to Equation (9) for finding the correct reference chart reduced pressure to use. This is easily found as follows:
By definition

Oscar T. Bloomer, is with the Eastman Kodak Company, Rochester, New York.

$$d'_r = (P_r/T_r)(Z'_c/Z) \quad (10)$$

It is required that

$$d'_{r(c)} = d'_{r(c)}$$

and

$$Z_{(c)} = Z_{(c)}$$

Hence

$$P_{r1}/T_{r1} = P_{r2}/T_{r2} \quad (11)$$

or

$$P_{r1}/P_{r2} = T_{r1}/T_{r2} \quad (12)$$

which is the desired relationship.

Equation (9) can be rearranged into the following form:

$$P'_r/P_r = T'_r/T_r = (S' - Z'_c)/[(S - Z'_c) + T_r(S' - S)] \quad (13)$$

Here those symbols with the superscript refer to the reference substance and those without the superscript refer to the gas whose properties are desired. This equation is plotted for a series of constant values of S in Figure 1. For this plot Z'_c was taken as 0.2900, and $S' = 1.8329$. The latter is the value of the slope of the pseudocritical isometric in dimensionless form for nitrogen. This plot is thus intended for use with a generalized compressibility-factor chart based on the PVT data of nitrogen. A generalized chart for nitrogen is presented in Figure 3. (The low pressure region of this chart is presented in Figure 2.)* This chart covers the reduced-temperature range 0.75 to 3.0 and the reduced-pressure range 0.0 to 10.0. The compressibility factor is plotted as a function of the pseudoreduced density in Figure 4. It is important to remember when using Figure 4 that the pseudoreduced density is not multiplied by the correction factor. The data and method used for the construction of these charts are discussed in an unpublished thesis (2). The charts were restricted to a reduced temperature of 3.0 because experimental data much above this temperature are available only for such gases as hydrogen and helium. Accurate extrapolation cannot be based on these gases because quantum effects are important for these gases.

PROCEDURE FOR USING THE CORRELATION

To find the compressibility factor of a gas at a given pressure and temperature with Figures 1, 2, and 3 used, the following procedure is followed:

1. Using the known values of the critical pressure and temperature of the substance one can calculate the reduced temperature (T/T_c) and reduced pressure (P/P_c) for the gas at the desired condition of pressure and temperature.

2. Using the known value of S for the substance, one can determine the ratio $T'_r/T_r = P'_r/P_r$ from Figure 1 or Equation (13).

3. One can multiply the values of the reduced temperature and pressure for the substance (step 1) by the ratio determined in step 2. This gives the corrected reduced temperature and reduced pressure to be used with the reference substance Z chart.

4. One should look up the value of Z on the reference substance chart (Figures 2 or 3) using the corrected reduced temperature and reduced pressure determined in step 3.

When the density instead of the pressure is known, the pseudoreduced density is calculated from the equation $d_r = d/d'_c = 0.29 RT_c d/P_c$. Then Figure 4 is used to determine the compressibility factor. Note that d_r is not multiplied by the correction factor.

Values of S for a number of pure gases are presented in Table 1. A correlation for predicting S when it is not known is presented in the following section.

DETERMINATION OF THE PARAMETER S

The parameter S is readily determined from experimental PVT data

when they are available. Only one isotherm is required. The data along the isotherm are interpolated to find the pressure at the pseudocritical density. The slope of the critical isometric is then found from

$$s = \frac{P - P_c}{T - T_c}$$

Then

$$S = \frac{s}{Rd'_c} \quad (8)$$

Since the pseudocritical isometric is not quite linear at temperatures well removed from the critical temperature, the value of S will depend slightly on the isotherm used to determine it. The values of S tabulated in Table 1 are based on experimental data for the isotherm nearest to a reduced density of 1.40. For the higher hydrocarbons the highest temperature investigated was well below 1.4, and for these gases the highest experimental isotherm was used. It is believed that the maximum error in S resulting from using isotherms higher or lower than $T_r = 1.4$ to determine it will not exceed 1%.

For those gases where there are no experimental PVT data available, it is necessary to have a reliable means of predicting them. It has been found that the parameter S can be related to the

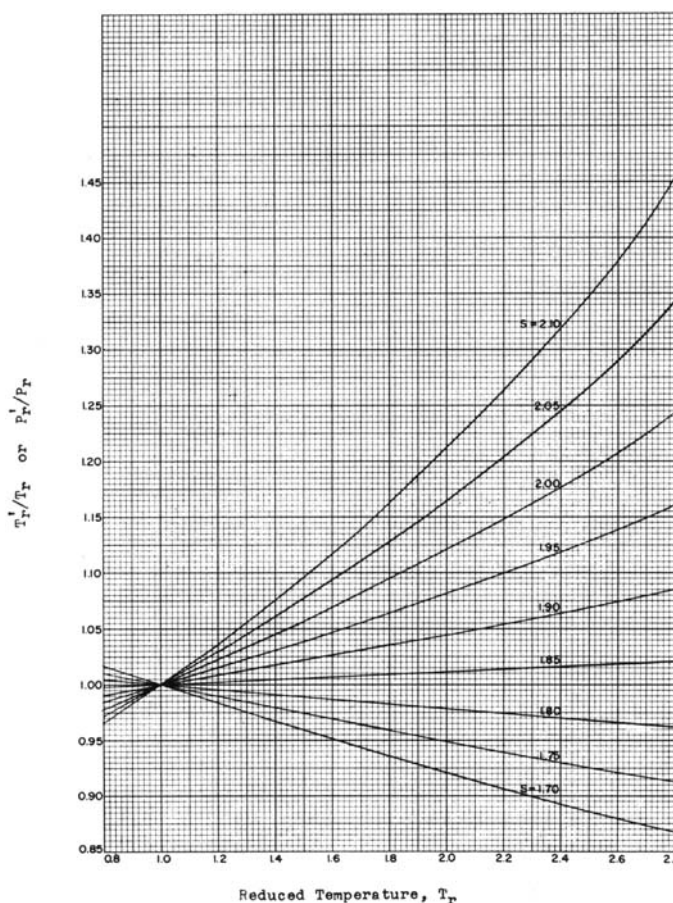


Fig. 1. Chart for determining the corrected reduced temperature and corrected reduced pressure.

* Larger scaled copies of the drawings in this paper can be obtained from the authors.

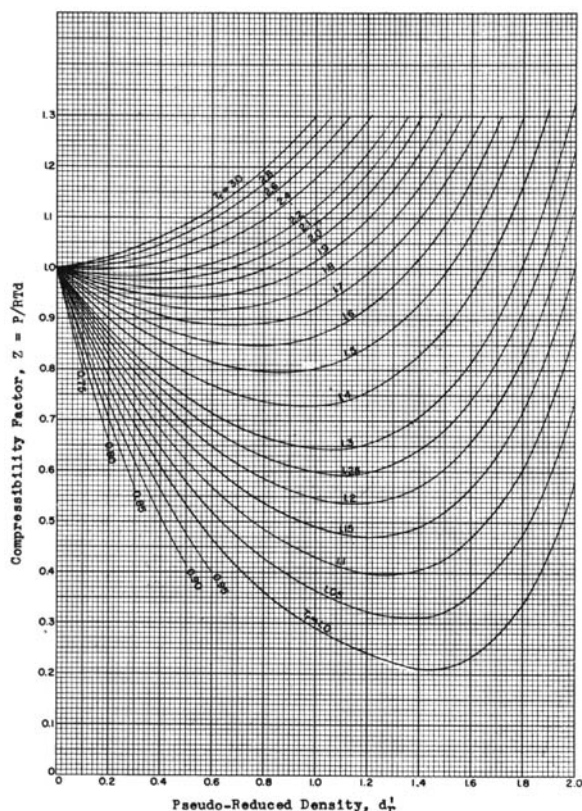


Fig. 4. Compressibility factor vs. pseudoreduced density.

Webb, and Ruben (1) the effect of density (at constant temperature) on the thermodynamic properties of a real gas can be expressed in terms of the residual work content \bar{A} , which may be evaluated from the following gas law deviation function:

$$\bar{A} = \int_0^d [(P - RTd)/d^3]_T \delta d \quad (14)$$

A function of \bar{A} is also required. This is the residual entropy function \bar{S}_a , which may be evaluated from

$$\bar{S}_a = - \left(\frac{\partial \bar{A}}{\partial T} \right)_d \quad (15)$$

From the definition of \bar{A} one sees that

$$\frac{\bar{A}}{RT} = \int_0^d \left(\frac{P}{RTd} - 1 \right) (1/d) \delta d = \int_0^d (Z - 1)/d \delta d \quad (16)$$

or in a dimensionless form

$$\frac{\bar{A}}{RT} = \int_0^{d_r^*} (Z - 1)/d_r^* (\delta d_r^*) \quad (17)$$

Now if a plot of Z vs. d_r^* for two gases coincides along a given reduced-temperature isotherm, then the above integral will coincide for the two gases at all values of d_r^* . It is evident that a chart of the dimensionless function \bar{A}/RT vs. d_r^* with lines of constant T_r for a given gas can be used for a sec-

ond gas provided that the corrected reduced temperature is used instead of the true reduced temperature. Thus the method of using this chart would be the same as for the compressibility-factor chart.

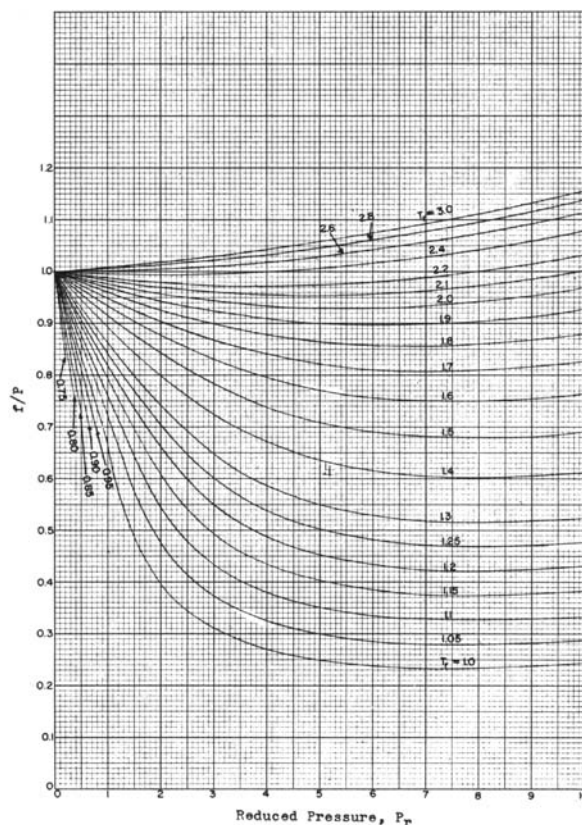


Fig. 5. Generalized chart for determining the fugacity to pressure ratio.

When one considers \bar{S}_a , from Equations (14) and (15)

$$\bar{S}_a = - \int_0^d \left(\frac{\partial P}{\partial T} \right)_d - Rd \quad (18)$$

TABLE I. CORRELATION OF THE PARAMETER S WITH THE RATIO T_c/T_b

Gas	Critical temperature, °K.	Critical pressure, atm.	Pseudo-critical density g.-moles/liter	s/Rd'	Normal boiling temperature, °K.	T_c/T_b	s/Rd'_c T_c/T_b
Nitrogen	126.26	33.54	11.163	1.8329	77.36	1.632	2.995
Krypton	209.39	54.27	10.892	1.7623	120.26	1.741	3.065
Xenon	289.81	57.89	8.396	1.7700	166.06	1.745	3.09
Methane	190.56	45.50	10.040	1.7920	111.66	1.706	3.06
Ethane	305.43	48.20	6.631	1.8570	184.86	1.652	3.07
Propane	370.00	42.01	4.771	1.8951	230.99	1.602	3.04
n-Butane	425.17	37.48	3.704	1.9370	272.67	1.559	3.02
iso-Butane	408.14	36.00	3.707	1.9640	262.96	1.552	3.05
N-Pentane	469.78	33.31	2.980	1.9897	309.36	1.519	3.025
neo-Pentane	433.76	31.57	3.058	1.9660	282.66	1.534	3.015
n-Heptane	540.17	27.00	2.095	2.0520	371.68	1.453	2.98
Ethylene	282.41	50.05	7.447	1.8510	169.26	1.668	3.085
Propylene	364.56	45.40	5.233	1.8906	225.46	1.617	3.065
iso-Butylene	417.89	39.48	3.970	1.9374	267.16	1.564	3.03
Carbon Dioxide	304.16	72.90	10.072	1.9450	183.81†	1.655	3.215
Oxygen*	154.66	49.71	13.520	1.8115	90.16	1.715	3.10
Hydrogen*	33.19	12.98	16.434	1.565	20.42	1.626	2.55
Hydrogen Sulfide	373.56	88.87	9.998	1.845	213.56	1.749	3.225
Water†	647.3	218.2	14.170	2.010	373.16	1.735	3.485

* Based on data at 100 atm. and 0°C.; reduced density = 0.3575 and hence should be rechecked when new data is available at higher densities.

† At 17.17°K. the vapor pressure of hydrogen is equal to one-fortieth of the critical pressure. When one uses this value for T_b , the product $S \times T_c/T_b$ is equal to 3.025.

‡ Because of the high triple-point pressure of carbon dioxide the liquid phase is not stable at 1-atm. pressure. This value for the normal boiling point was obtained by extrapolation of the vapor-pressure curve for the liquid phase.

† The PVT correlation is not recommended for water.

or in dimensionless form

$$\frac{\bar{S}_d}{R} = - \int_0^{d_r} \left[\left(\frac{\partial P}{\partial T} \right)_d / R d - 1 \right] \frac{1}{d_r} \delta d_r \quad (19)$$

The term in the bracket is equal to $S - 1$ when the density is equal to the pseudocritical density. Thus the value of this quantity for two gases at the pseudocritical density is in the ratio of $(S - 1)_2 / (S - 1)_1$. It was found from experimental PVT data that this ratio applies for the term in the bracket at all densities within the limit of the correlation. Hence

$$\left(\frac{\bar{S}_d}{R} \right)_2 = \frac{(S - 1)_2}{(S - 1)_1} \left(\frac{\bar{S}_d}{R} \right)_1$$

The effect of pressure (or density) on the thermodynamic functions of the real gas can be obtained from the two functions \bar{A}/RT and \bar{S}_d/R for the reference gas nitrogen with the following equations used:

$$(S_{d,T} - S^*_T)/R =$$

$$[(S - 1)/0.8329] \bar{S}_d/R - \ln P/Z \quad (20)$$

$$(H_{d,T} - H^*_T)/RT =$$

$$[(S - 1)/0.8329] \bar{S}_d/R + \bar{A}/RT + (Z - 1) \quad (21)$$

$$(E_{d,T} - E^*_T)/RT =$$

$$[(S - 1)/0.8329] \bar{S}_d/R + \bar{A}/RT \quad (22)$$

$$(A_{d,T} - A^*_T)/RT = \bar{A}/RT + \ln P/Z \quad (23)$$

$$(F_{d,T} - F^*_T)/RT =$$

$$\ln f = \bar{A}/RT + \ln P/Z + (Z - 1) \quad (24)$$

The functions \bar{S}_d/R and \bar{A}/RT for

TABLE 2. SUMMARIZED COMPARISON OF PROPOSED CORRELATION WITH EXPERIMENTAL DATA FOR TWELVE GASES

Gas	Average % error up to a pseudoreduced density of 1.0		Average % error up to a pseudoreduced density of 1.2		Maximum error of any point up to a reduced density of 1.2		Reduced temperature range of experimental data
	Proposed correlation	Without the parameter S	Proposed correlation	Without the parameter S	Proposed correlation	Without the parameter S	
Xenon	0.14	1.11	0.17	1.33	0.85	3.95	1.000-1.977
Nitrogen			basis of correlation				0.750-3.000
Krypton	0.15	1.72	—	—	0.69	3.34	1.305-2.737
Methane	0.22	1.08	0.30	1.22	1.76	3.04	1.066-2.483
Ethane	0.27	0.51	0.32	0.49	0.87	1.36	0.976-1.713
Propane	0.28	1.22	0.33	1.22	1.19	2.94	1.000-1.511
n-Butane	0.23	1.35	—	—	0.65	4.45	0.995-1.348
n-Pentane	0.28	2.08	0.37	2.21	1.13	4.85	1.007-1.220
neo-Pentane	0.22	1.72	0.27	1.87	1.23	4.98	1.000-1.264
n-Heptane	0.44	2.77	0.55	2.93	1.16	5.98	1.015-1.154
Ethylene	0.25	0.45	—	—	0.83	1.05	0.967-1.670
iso-Butene	0.23	1.45	0.25	1.51	1.10	3.37	1.013-1.312
Hydrogen Sulfide	0.26	0.43	—	—	0.72	1.86	0.744-1.189
Average	0.25	1.32	0.32	1.60	1.01	3.43	

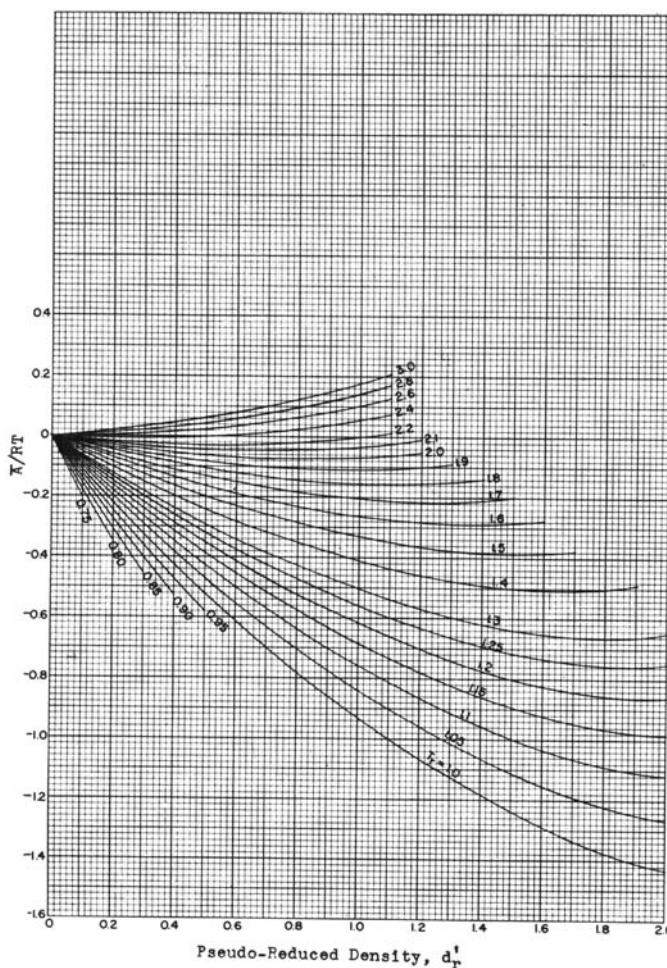


Fig. 6. Generalized chart for determining the residual work content.

nitrogen are plotted in Figures 6 and 7 against the pseudocritical density. The corrected reduced temperature and the pseudoreduced density are used with Figures 6 and 7 to determine the values of \bar{S}_d/R and \bar{A}/RT . However the value of \bar{S}_d/R must be corrected as noted in the equations. The value read from Figure 7 is multiplied by $(S - 1)/0.8329$. The 0.8329 term is the value of $S - 1$ for the reference gas nitrogen.

Figure 5 plots the commonly used fugacity to pressure ratio chart vs. the pressure for nitrogen. The method of using this chart for other gases is the same as with the compressibility-factor chart. The corrected reduced temperature and corrected reduced pressure are used instead of the true values.

DISCUSSION

It is well known that the law of corresponding states applies rigorously only to the spherical nonpolar molecules. It is obvious that the correction factor S presented here takes into account the aspherical factor for nonpolar molecules. It thus may be regarded as a shape factor. If a polar molecule is very nearly spherical (as

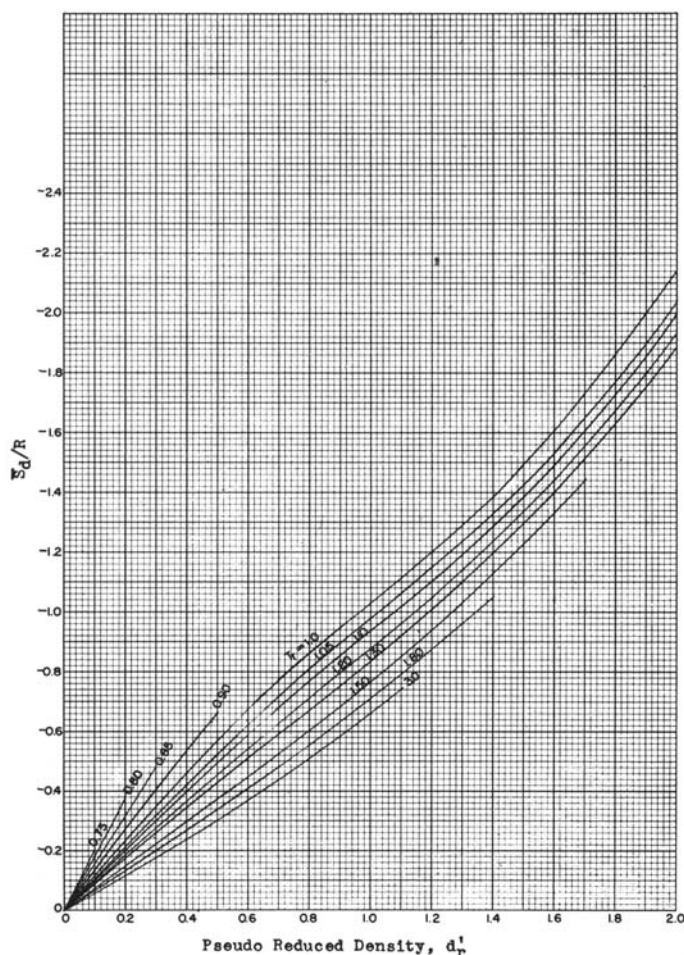


Fig. 7. Generalized chart for determining the entropy difference.

for example hydrogen sulfide), then the correction also does a good job of taking into account the dipole moment of the molecule. If the molecule is highly polar (as for example water) or both is aspherical and has a dipole moment (as for example the alcohols), then the correlation is probably not very satisfactory. However the later cases were not investigated in this work. Those few gases which have quantum correction were also not investigated, although it appears that the correlation should be satisfactory for them up to a reduced temperature of 3.0.

A correlation with a similar third parameter but different in the method of correcting for the third parameter has been presented by Pitzer *et al.* (6). They also related the third parameter to the vapor-pressure curve using a method very similar to that presented here. However the method presented here for taking into account the effect of the third parameter on the gas properties is considerably simpler to use and is at least as accurate over most of its range of applicability. The correlation of Pitzer *et al.* has a somewhat greater range of applicability.

The true critical point compressibility factor has also been proposed by

Meissner and Seferian (5) as a third parameter. The use of this quantity as the third parameter however suffers from the fact that accurate data are seldom available for it. However a very simple relationship between the parameter S and the critical point compressibility factor has been found for the gases investigated in this work: $S \times Z_c = 0.5280$.

With the exception of carbon dioxide, hydrogen, and water, the values of S calculated from this equation agree with those tabulated in Table 1 to within an average of 1.13%. The maximum error is 2.6%. The error for carbon dioxide is 4.2% ($Z_c = 0.283$). Thus Z_c should be a satisfactory third parameter for nonpolar gases. However the correlation of S as a function of the ratio T_c/T_b and the critical pressure is much preferred because these data are usually available and are of higher accuracy than Z_c . It would appear that the above equation is a satisfactory method for estimating Z_c for nonpolar gases when no experimental data are available.

NOTATION

A = work function per mole
 \bar{A} = difference between work con-

tent of real gas at given temperature and density and ideal gas at same temperature and density

E = energy content per mole
 F = free energy per mole
 H = enthalpy per mole
 I = intercept on P axis
 P = absolute pressure
 R = universal gas constant per mole
 S = entropy per mole, the slope of the pseudocritical isometric in dimensionless form ($s/R d'_c$)
 \bar{S}_d = difference between entropy of real gas and ideal gas at same temperature and density
 T = absolute temperature
 Z = compressibility factor
 d = molar density
 f = fugacity
 s = slope of the pseudocritical isometric

Subscripts

c = the critical state
 P, d, T = a constant pressure
 r = reduced state, a state relative to the critical state

Superscripts

$*$ = state of ideal gas-law behavior at 1-atm pressure
 $-$ = differences between the value of a property and the value of the property if the substance behaved as an ideal gas at the same temperature and density as the real gas
 $\bar{}$ = reduced quantity which has been corrected by the proposed correlation

Abbreviations and other symbols

∂ = partial differential operator
 \int = integral operator
 $\frac{d}{dx}$ = differential operator

LITERATURE CITED

1. Benedict, Manson, G. B. Webb, and L. C. Rubin, *J. Chem. Phys.*, **8**, 334 (1940).
2. Bloomer, O. T., Ph.D. thesis, Illinois Inst. Tech., Chicago (June, 1954).
3. Cope, J. Q., W. K. Lewis, and H. C. Weber, *Ind. Eng. Chem.*, **23**, 887 (1931).
4. Curtis, C. F., C. A. Boyd, and H. B. Palmer, *J. Chem. Phys.*, **19**, 663 (1951).
5. Meissner, H. P., and R. Seferian, *Ind. Eng. Chem.*, **27**, 302 (1935).
6. Pitzer, K. S., D. Z. Lippmann, R. F. Curl, C. M. Huggins, and D. E. Petersen, *J. Am. Chem. Soc.*, **77**, 3433 (1955).
7. Su, G. J., *Ind. Eng. Chem.*, **38**, 803 (1946).

Manuscript received March 17, 1959; revision received July 27, 1959; paper accepted August 4, 1959.