

# Compressibility Chart for Hydrogen and Inert Gases

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WITH industrial processes using high pressure hydrogen, helium, neon, and argon becoming common, there is a great need for an accurate compressibility chart of these gases. The generalized compressibility chart commonly used (2) is highly inaccurate for the above gases. Newton (9) found that an empirical correction quantity of 8 added to both the critical temperature,  $T_c$ , and critical pressure,  $P_c$ , of hydrogen, helium, and neon allowed the use of his generalized activity coefficient chart with a fair degree of accuracy. Dodge (2) suggested using the same quantities for the generalized compressibility chart. However, lately it has been shown that these quantities are only accurate over very limited ranges of temperature and pressure (8). In other

regions of temperature and pressure, sizable errors result from the use of the Newton correction quantities.

In view of this, a compressibility chart for hydrogen has been constructed, and the data for the inert gases fitted to it. Many of the hydrogen  $P$ - $V$ - $T$  data were obtained from the excellent National Bureau of Standards paper (11) summarizing hydrogen data up to 1941. Additional data for pressures below  $P_R = 10$  were obtained from (6) and (12). Data for pressures to  $P_R = 130$  for  $T_R$  ranging from 2.00 to 15.00 were obtained from (6, 7, 11, 12). Although (7) was used in the Bureau of Standards summary (11), it also contains data at higher pressures than given in (11). For example, (7) gives values to  $P_R = 92.6$  at  $T_R = 8.95$ , while (11) only goes to  $P_R = 65.7$  at  $T_R = 9.04$ . These high  $P_R$  values of (7) were checked with those of (6). Data for the region  $T_R = 2.00$  to 8.00 and  $P_R = 40$  to 130 were largely obtained from (6)

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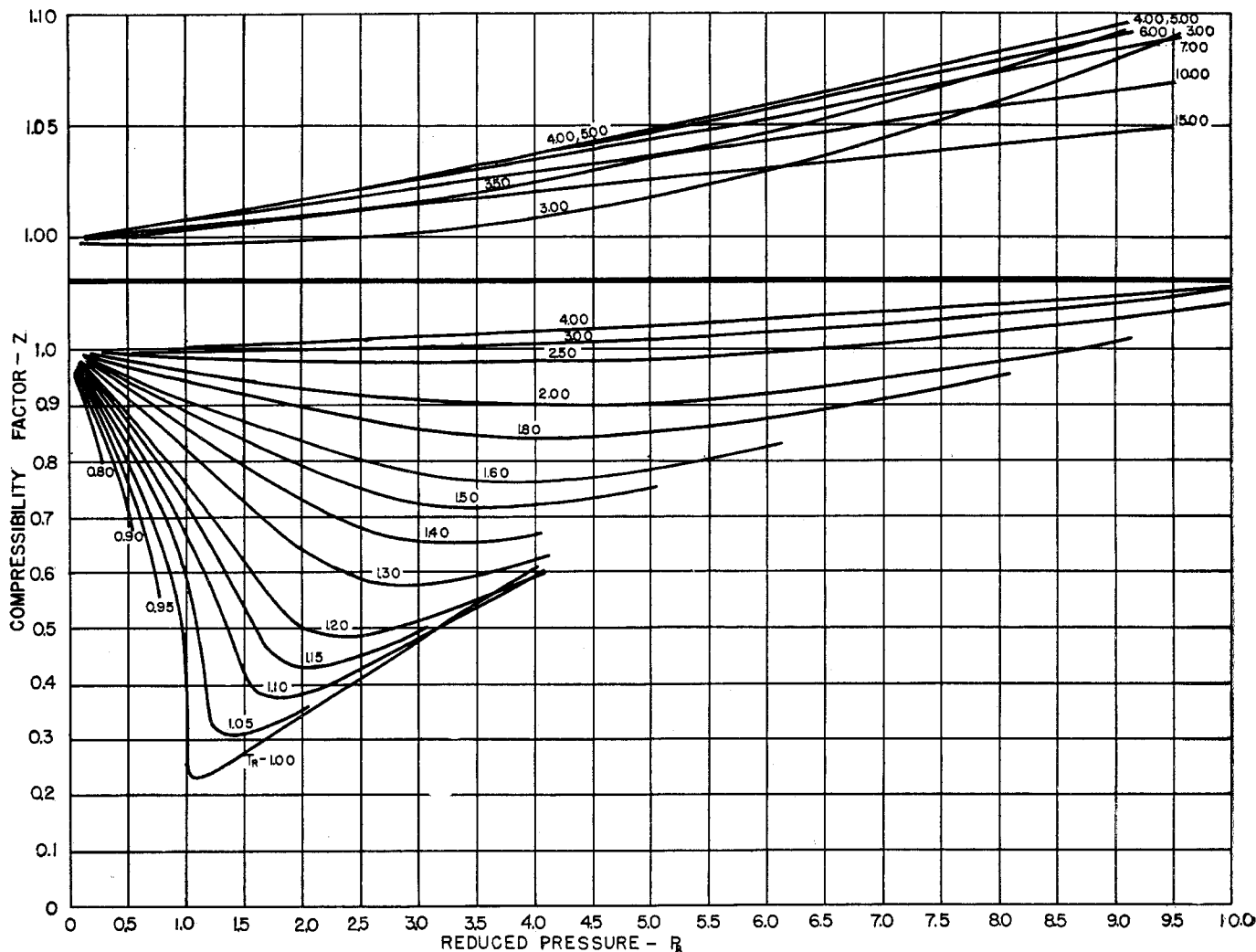


Figure 1. Compressibility Chart--Low Pressure Range

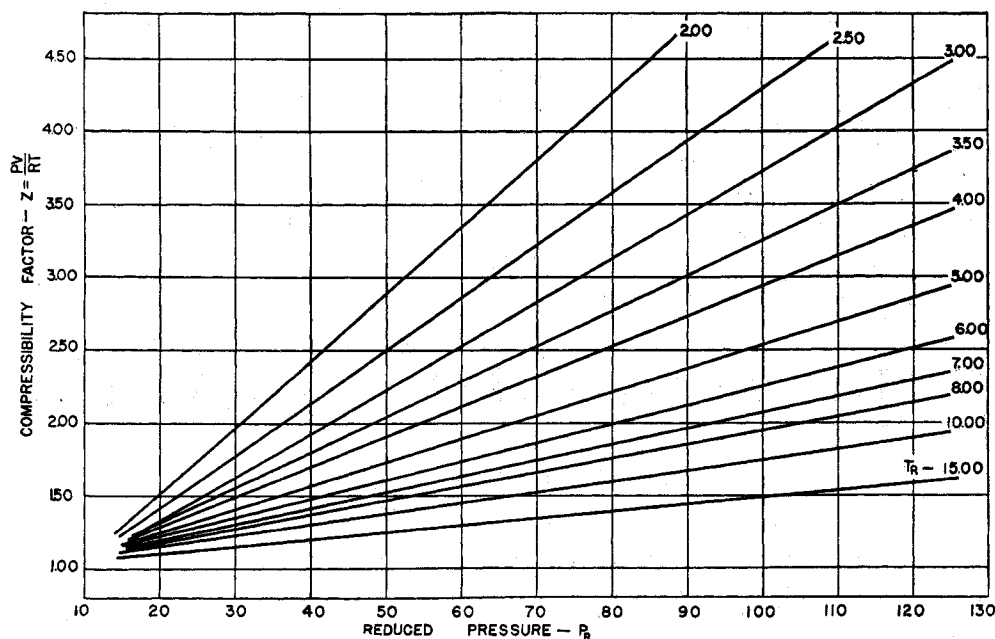


Figure 2. Compressibility Chart—High Pressure Range

and (12), since (11) gives little data in this range. In all cases the data were carefully examined for self-consistency.

The National Bureau of Standards revisions of the critical constants for hydrogen (11) were adopted and are given in Table I, together with the accepted constants for the inert gases.

TABLE I. GAS CONSTANTS

	Critical Temp., ° K.	Critical Pressure, Atm.	Critical Constant Corrections	
			Temp., ° K.	Pressure, Atm.
Hydrogen	33.19	12.98	...	...
Helium	5.22	2.26	+1.2	+1.3
Neon	44.42	25.9	-3.2	-0.8
Argon	151.12	48.0	-7.4	+2.5

$P$ - $V$ - $T$  data for the inert gases (1, 3-5, 10) are fairly meager. Of the existing helium data, a large portion is at values of  $T_R$  and  $P_R$  much higher than the range covered in this paper. This is due to the very low critical constants for helium. However, enough data are available to permit evaluation of pseudocritical constants over a range of conditions. Practically all of the neon and argon data are for  $P_R$  less than 10.00. In this region there is sufficient data for a reasonably good evaluation of pseudocritical constants. For each gas all of the data were examined and plotted so as to give the best self-consistent correlation.

The final compressibility charts, Figures 1 and 2, are based on this hydrogen data and are exact for hydrogen. They cover a range of conditions up to 500° K. and 1000 atmospheres. These charts were constructed by plotting all of the good and self-consistent hydrogen data, and then cross-plotting so as to obtain charts having curves at the values of  $T_R$  shown. In every case, care was taken to use a large enough scale so as to retain all of the original accuracy. Some of the curves at low values of  $T_R$  are incomplete. This is due to the lack of experimental data in this region.

Figure 1 includes an expansion of the upper portion of the chart. This allows greater reading accuracy in a region where many curves cross one another. This enlargement shows more clearly than previous charts that, at constant  $P_R$ , as the value of  $T_R$  increases the compressibility factor ( $Z = PV/RT$ ) reaches a

maximum and then decreases. Thus, permanent gases, even under high pressures, tend to approach ideal gas behavior as the temperature is increased.

#### INERT GASES

The compressibility data for the inert gases were fitted to the hydrogen curves, and simple empirical additive corrections for  $T_c$  and  $P_c$  were determined. These are given in Table I. No special theoretical significance is attached to their values.

While more complex correlating methods showing the variation of the critical constant corrections with reduced temperature and pressure possibly could be used, the limited amount of experimental data available does not warrant it.

Even if this were done, there would be only a slight variance in the corrections, since the reduced  $P$ - $V$ - $T$  behavior of the inert gases is so similar to that of hydrogen. For example, Morgen and Childs (8) showed that hydrogen, helium, and neon had practically identical deviations from the generalized compressibility charts and actually found that a single correction curve sufficed for all three gases.

As an example of the use of the corrections, the pseudocritical constants for helium for these charts are:

$$T_c + 1.2 = 6.42 \text{ and } P_c + 1.3 = 3.56.$$

#### ACCURACY OF THE CHARTS

The three charts are exact for hydrogen. Their accuracy for the inert gases when the pseudocritical constants are used varies depending on the gas and on the particular pressure and temperature in question. In Table II some representative comparisons covering the range of experimental data are given. These show an average error in the compressibility factor,  $Z$ , of 1.4%. The largest deviations occur in the critical region, as may be expected, since the severest test of this type of correlation occurs there (2).

#### ACKNOWLEDGMENT

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TABLE II. COMPARISON OF EXPERIMENTAL DATA FOR INERT GASES WITH COMPRESSIBILITY CHARTS

	Temp., ° K.	Pressure, Atm.	Compressibility Factor, $Z = \frac{PV}{RT}$	
			Experimental	Chart using pseudocritical constants
Helium	14.34	15.4	0.935	0.944
	20.47	12.4	0.998	1.000
	67.81	47.61	1.090	1.095
Neon	60.04	59.77	0.712	0.730
	90.5	41.37	0.964	0.950
	293.1	82.54	1.040	1.030
Argon	157.26	41.9	0.673	0.700
	215.4	35.1	0.925	0.917
	293.5	61.7	0.970	0.956

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# Binary Vapor-Liquid Equilibria

## Trial and Error Prediction and Correlation

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IN ORDER to predict distillation phenomena and to design distillation equipment, it is necessary to have information on vapor-liquid equilibrium for the system under consideration. A great variety of apparatus for obtaining vapor-liquid equilibrium data by direct experiment has been described.

It is often difficult to obtain equilibrium samples from such an apparatus, and to analyze these samples with the required precision and accuracy. It has become standard practice to test the consistency of vapor-liquid equilibrium data obtained with such apparatus, by procedures based on thermodynamic equations derived from the Gibbs-Duhem equation. For this purpose, additional information, such as the vapor pressure-temperature relationships of the pure compounds and the boiling point-composition diagram of the mixture, is required.

It has long been recognized that the ability to predict the equilibrium data from such additional information only would be of great value. Various methods of prediction for binary systems (1-3, 5, 6, 11-13, 15, 16, 19, 23-26) have been proposed, but these are usually applicable only when the mixture under consideration behaves in accord with some particular simplified thermodynamic equation. The method proposed in this paper is more general. It involves a straightforward trial and error procedure, and makes use of such information as boiling point-composition data, vapor pressure-temperature data on the pure components, and a thermodynamic equation applicable to the system. For the systems tested, it has been possible to obtain industrially useful results with moderate effort, and excellent results with more effort but with no increase in mathematical complexity. The method is most useful for systems that behave in accord with the van Laar or Margules equations, or equally simple equations. When more complex thermodynamic equations are required, the method is applicable in principle, but excessive computation is required. Fortunately, a great many common systems follow the van Laar, Margules, or similar equations.

The following calculation outlines and illustrates the method in its simplest form.

### PREDICTION OF ISOBARIC VAPOR-LIQUID EQUILIBRIA OF ETHYL ALCOHOL-WATER AT ATMOSPHERIC PRESSURE

**1. Boiling Point-Composition Data** from several sources for ethyl alcohol-water at 760 mm. of mercury were plotted, and found to be in close agreement (see Figure 1). The visually

smoothed data of Carey and Lewis (4) were used for the calculation. Vapor pressure-temperature data for ethyl alcohol (8) and water (10) were also plotted and visually smoothed.

If extreme precision had been desired, the smoothing would have been done by the method of least mean squares.

**2. Base Point.** The boiling temperature ( $t = 79.85^\circ \text{C.}$ ) of a 0.50 mole fraction ethyl alcohol solution and the vapor pressures ( $P_{oa} = 800$  mm. of mercury,  $P_{ob} = 353$  mm. of mercury) of the pure components at the boiling point were read from the graphs.

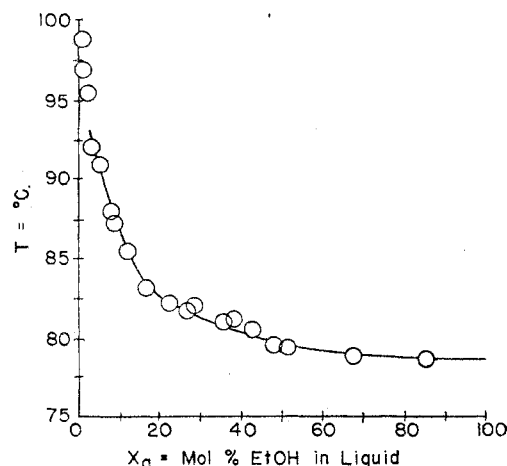


Figure 1. Ethyl Alcohol-Water at 760 Mm. of Mercury

○. Experimental (7, 14)  
— Carey and Lewis (4)

This particular liquid composition is referred to below as the "base point." The purpose of the ensuing procedure (steps 3 to 9) is to find, by trial and error repetition of these steps, the "correct" value of the equilibrium vapor composition at the base point liquid composition. "Correctness" here implies consistency with the experimental vapor pressure and boiling point data and with the thermodynamic equation that has been chosen as applicable. When the correct equilibrium vapor composition for this base point is established, the other equilibrium vapor compositions are obtained by step 10 of the procedure.