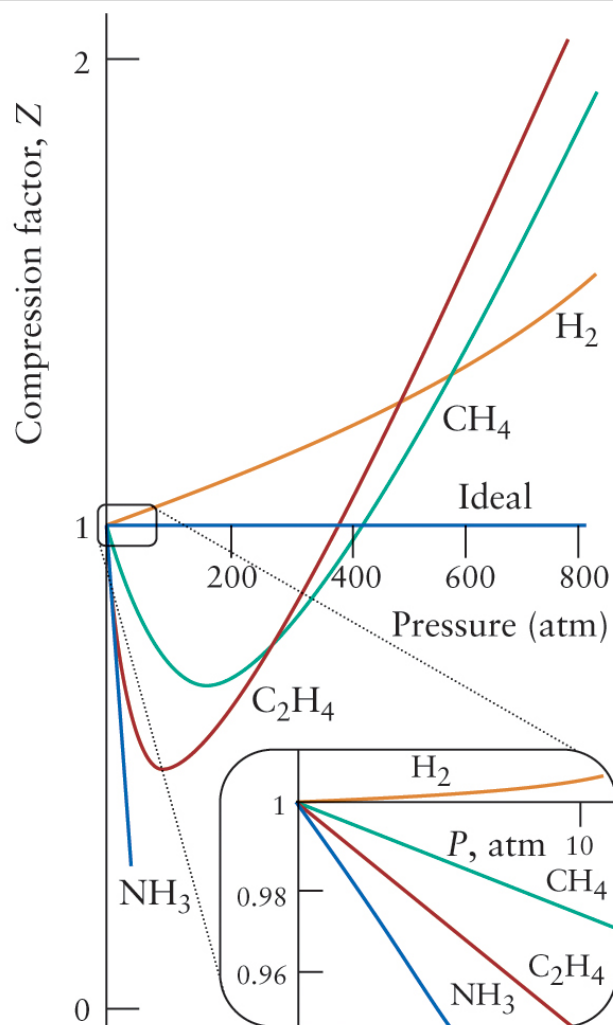
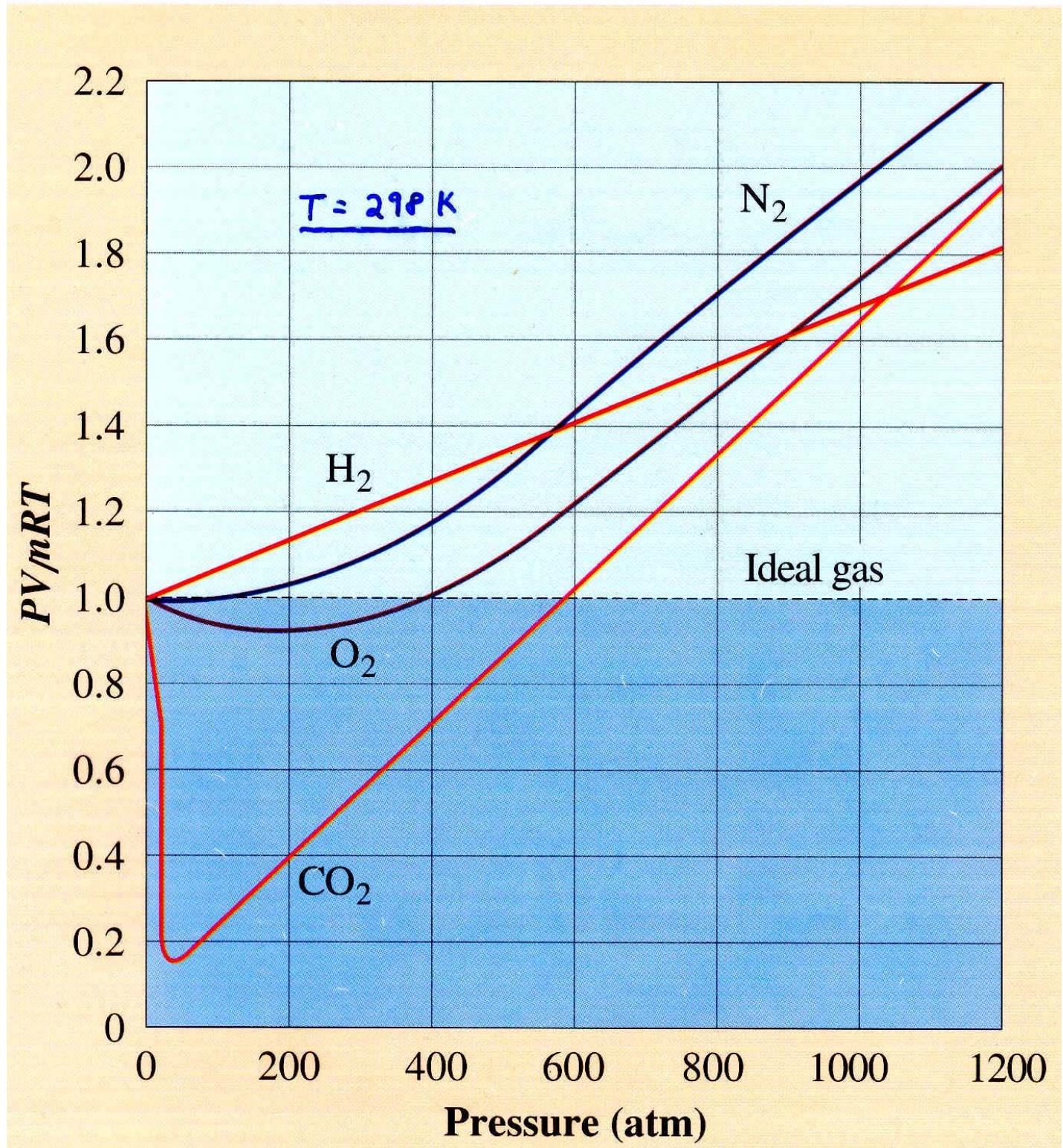


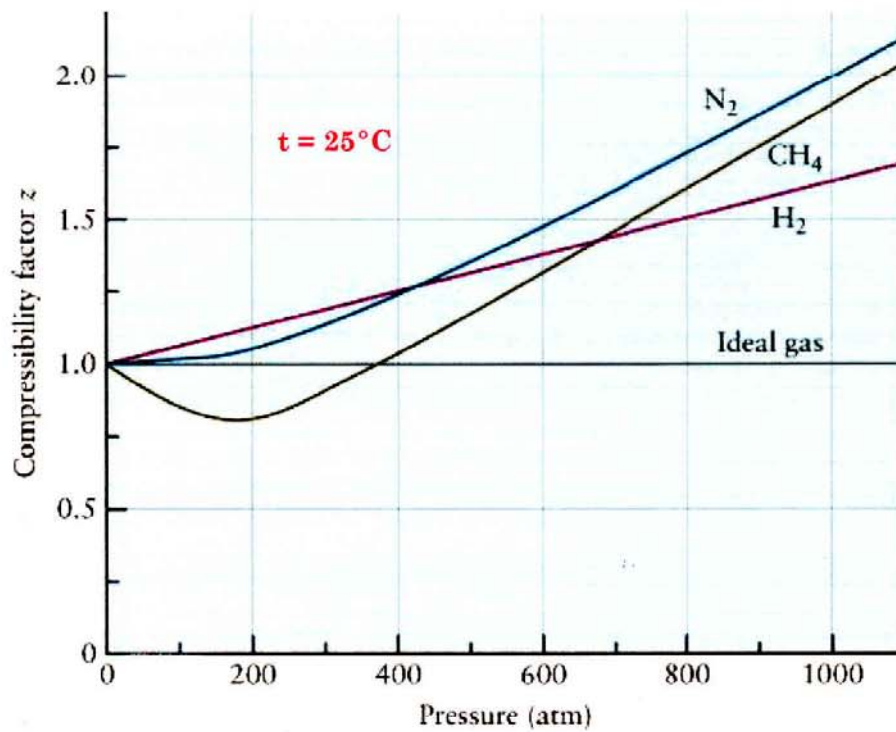
## Topic 3E - Real Gases



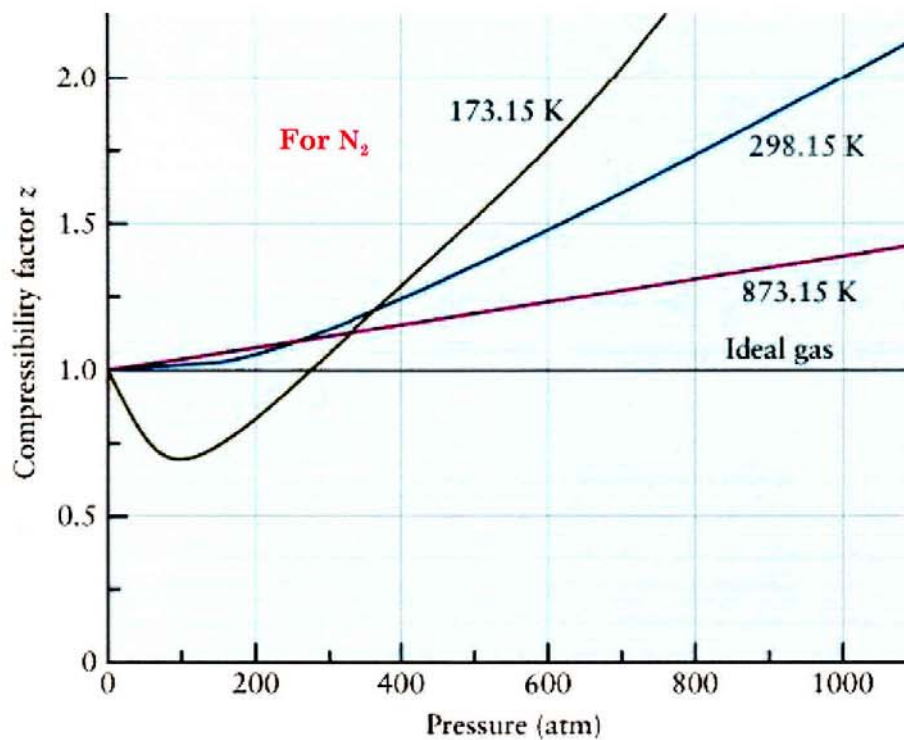
**FIGURE 5.28** A plot of the compression factor,  $Z$ , as a function of pressure for a variety of gases. An ideal gas has  $Z = 1$  for all pressures. For a few real gases with very weak intermolecular attractions, such as  $\text{H}_2$ ,  $Z$  is always greater than 1. For most gases, at low pressures the attractive forces are dominant and  $Z < 1$  (see inset). At high pressures, repulsive forces become dominant and  $Z > 1$  for all gases.

## Deviations from Ideal Gas Behavior



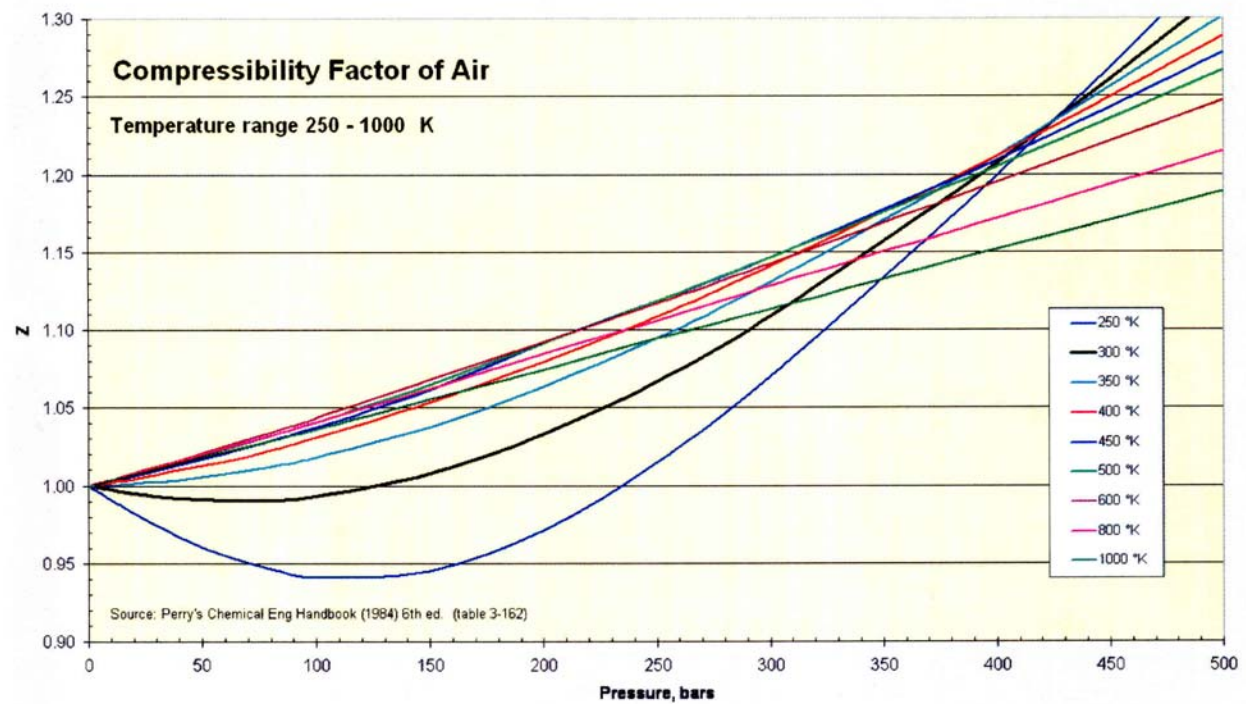
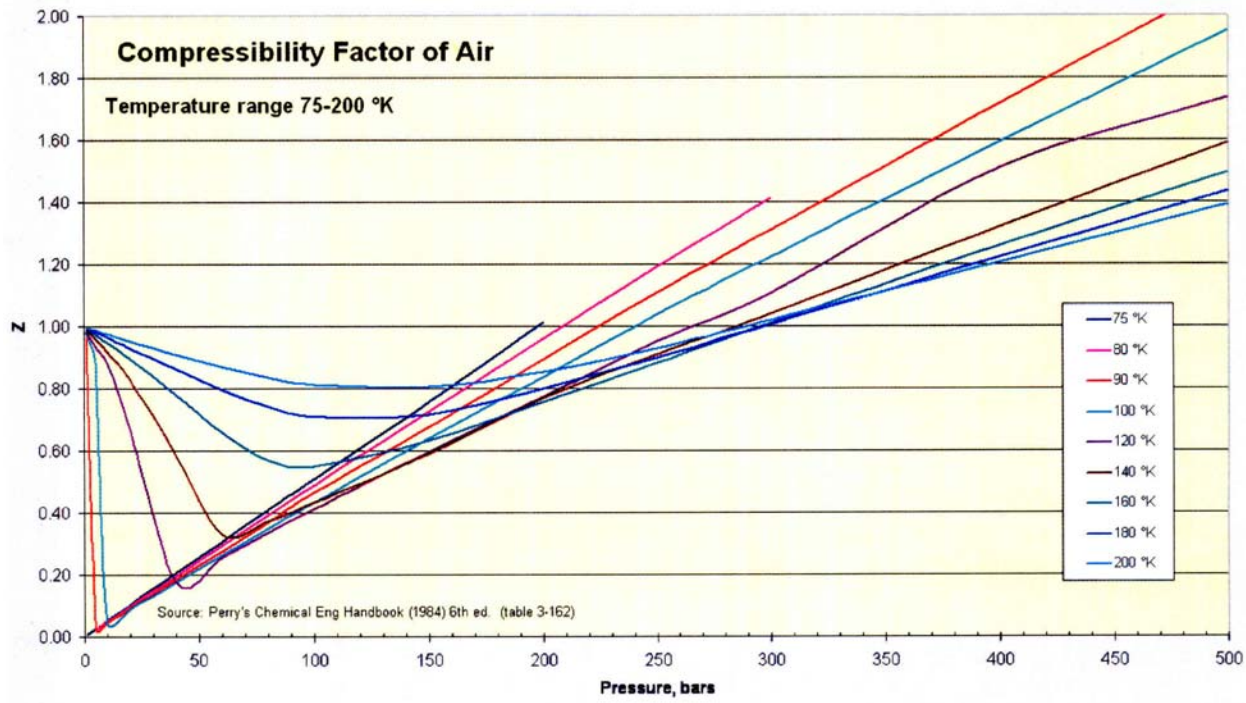


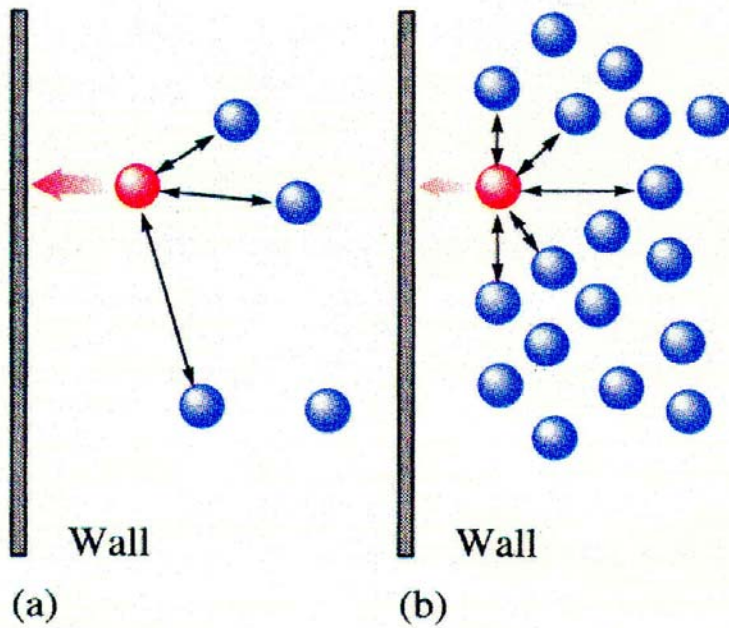
(a)



(b)

**FIGURE 9.17** A plot of  $z = PV/nRT$  against pressure shows deviations from the ideal gas law quite clearly, for an ideal gas,  $z$  is represented by the straight horizontal line. (a) Deviation of several real gases at  $25^\circ\text{C}$ . (b) Deviation of nitrogen at several temperatures.

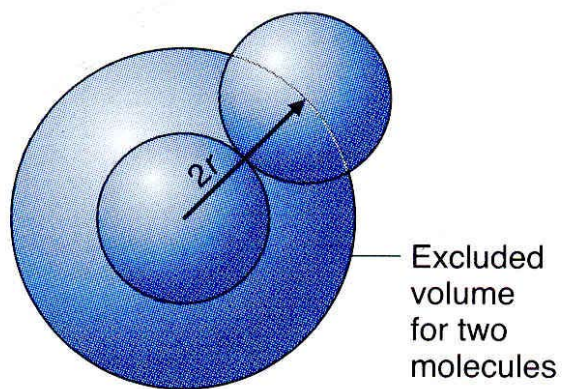




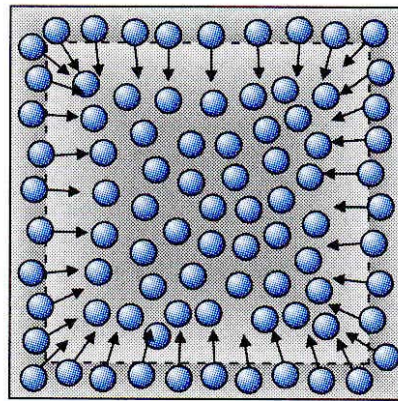
**Figure 5.25**

(a) Gas at low concentration—relatively few interactions between particles. The indicated gas particle exerts a pressure on the wall close to that predicted for an ideal gas.

(b) Gas at high concentration—many more interactions between particles. The indicated gas particle exerts a much lower pressure on the wall than would be expected in the absence of interactions.



**(a)** Excluded volume



**(b)** Attractive intermolecular forces

**Figure 6.2.** The physical basis for the van der Waals equation of state for a nonideal gas.

## Van der Waals Equation of State

To model real gases, the volume occupied by the gas particles themselves must be taken into account:

$$P' = \frac{nRT}{V - nb}$$

where the constant **b** is related to the molar volume of the gas particles.

Must also account for interparticle attractions among the gas particles, which effectively act to decrease the observed pressure:

$$P_{\text{obs}} = P' - a \left( \frac{n}{V} \right)^2$$

where the constant **a** is a quantitative measure of the potential energy of gas particle interactions.

Thus, applying both the “volume effect” and the “interaction effect” to the ideal gas law gives:

$$P_{\text{obs}} = \frac{nRT}{V - nb} - a \left( \frac{n}{V} \right)^2$$

which can be rearranged to the usual form of the van der Waals Equation of State:

$$\left[ P + a \left( \frac{n}{V} \right)^2 \right] (V - nb) = nRT$$

(corrected pressure)
(corrected volume)

For the ideal gas equation of state, the so-called compressibility factor,  $z$ , is given by:

$$z = \frac{PV}{nRT} = 1 \quad (\text{for an ideal gas})$$

and equals unity.

For the van der Waals' equation of state, the compressibility factor is:

$$z = \frac{PV}{nRT} = \frac{V}{V - nb} - \frac{a n}{RT V} = \frac{1}{1 - b \frac{n}{V}} - \frac{a n}{RT V}$$

At low P and high T,  $n/V$  becomes small, and  $z$  approaches the ideal value of unity.

Repulsive forces, represented by the constant  $b$ , serve to increase  $z$ .

Attractive forces, represented by the constant  $a$ , serve to decrease  $z$ .



## Van der Waals Constants for Some Common Gases

Gas	<b>a</b> (atm-L <sup>2</sup> /mol <sup>2</sup> )	<b>b</b> (L/mol)	Molar Vol. of Liquid (L/mol)	Boyle Temp. (K) (a/Rb)	Expt.
He	0.034	0.0237	0.027	17	22
Ne	0.211	0.0171	0.017	150	122
Ar	1.35	0.0322	0.029	511	412
Kr	2.32	0.0398	0.039	710	575
Xe	4.19	0.0511	0.037		
H <sub>2</sub>	0.244	0.0266	0.029	112	110
N <sub>2</sub>	1.39	0.0391	0.035	433	327
O <sub>2</sub>	1.36	0.0318	0.028	521	406
CO	1.49	0.0399	0.035	456	352
NO	1.34	0.0279	0.024		
NO <sub>2</sub>	5.28	0.0442			
N <sub>2</sub> O	3.78	0.0442			
HCl	3.67	0.0408			
HBr	4.451	0.0443	0.029		
H <sub>2</sub> O	5.46	0.0305	0.018	2181	1250
NH <sub>3</sub>	4.17	0.0371		1370	995
CO <sub>2</sub>	3.59	0.0427	0.040	1025	715
Cl <sub>2</sub>	6.49	0.0562			
CH <sub>4</sub>	2.25	0.0428			
C <sub>2</sub> H <sub>6</sub>	5.49	0.0638			
C <sub>3</sub> H <sub>8</sub>	8.66	0.0845			
C <sub>4</sub> H <sub>10</sub>	14.47	0.1226	0.097		
C <sub>5</sub> H <sub>12</sub>	19.01	0.1460	0.115		
C <sub>2</sub> H <sub>4</sub>	4.47	0.0571		954	735

## Table 9.3: Properties of Real Gases

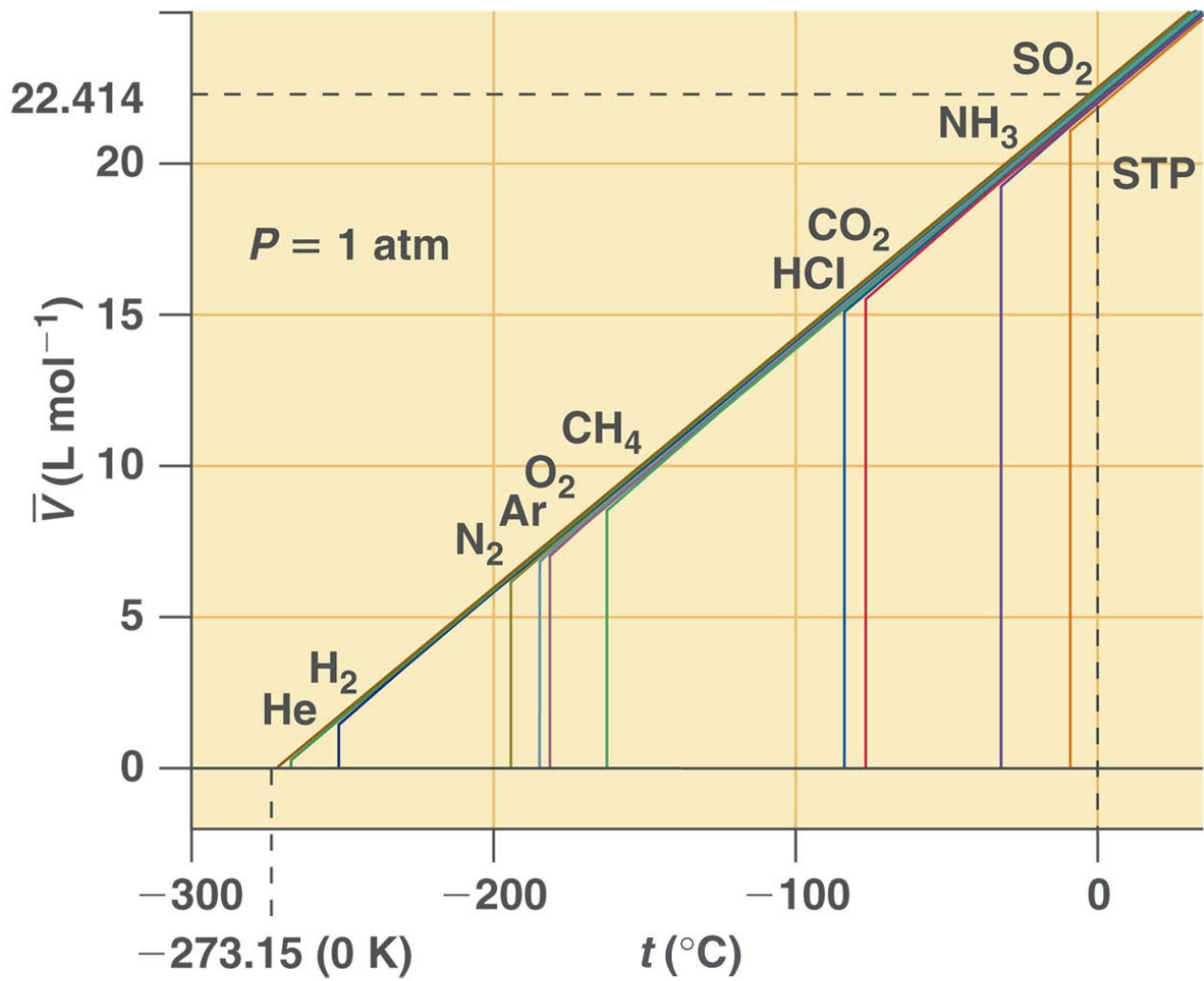
TABLE 9.3

### Properties of real gases

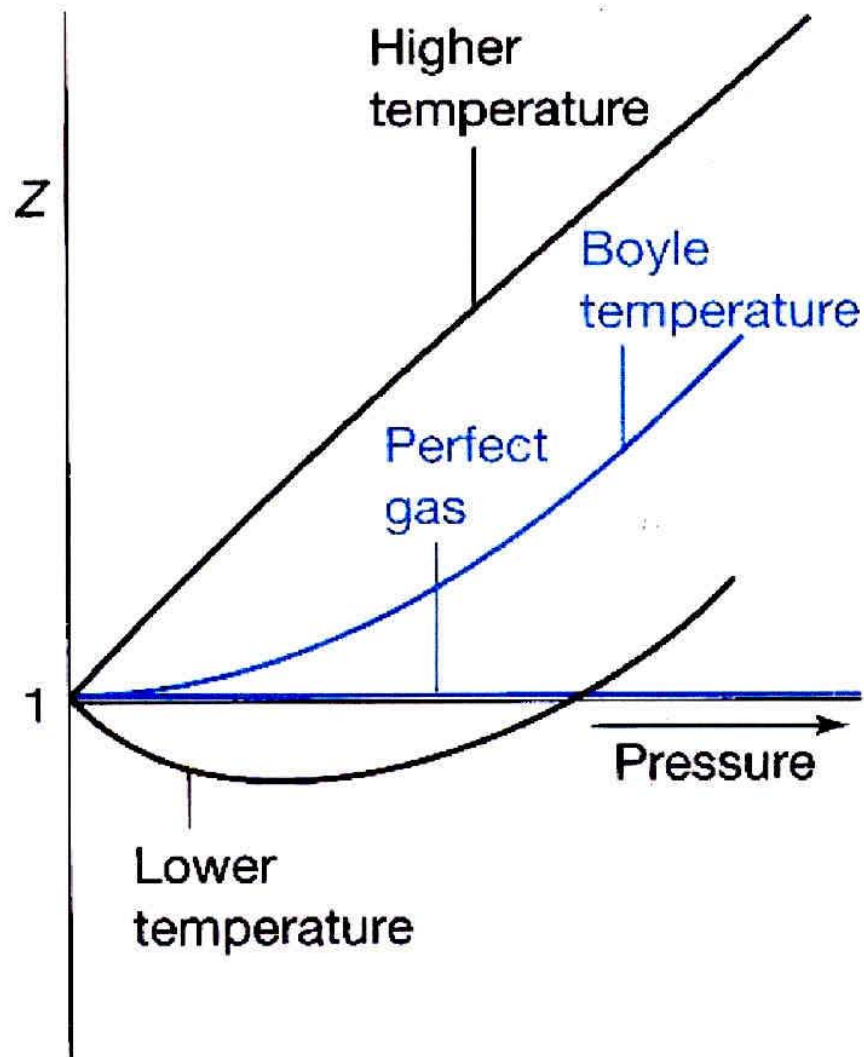
Gas	STP molar volume (L mol <sup>-1</sup> )	Boiling point at 1 atm $t_b$ (°C)	Van der Waals constants	
			$a$ (atm L <sup>2</sup> mol <sup>-2</sup> )	$b$ (L mol <sup>-1</sup> )
H <sub>2</sub>	22.419	-252.9	0.2421	0.02651
He	22.427	-268.9	0.0342	0.02376
Ne	22.414	-246.0	0.2056	0.01672
Ar	22.369	-185.7	1.337	0.03201
Kr	22.328	-152.3	2.295	0.03957
Xe	22.241	-107.1	4.138	0.05156
N <sub>2</sub>	22.373	-195.8	1.349	0.03860
O <sub>2</sub>	22.368	-183.0	1.364	0.03186
F <sub>2</sub>	22.376	-188.1	1.149	0.02876
Cl <sub>2</sub>	22.085	-34.6	6.501	0.05628
HF(g)	...	19.6	9.411	0.07371
HCl	22.251	-84.9	3.652	0.04061
HBr	22.196	-67.0	4.436	0.04436
HI	22.114	-35.6	5.747	0.04895
H <sub>2</sub> O(g)	...	100.0	5.463	0.03048
H <sub>2</sub> S	22.190	-60.7	4.478	0.04330
H <sub>2</sub> Se	22.140	-41.5	5.451	0.04789
NH <sub>3</sub>	22.176	-33.4	4.167	0.03711
PH <sub>3</sub>	22.207	-87.7	4.634	0.05157
CH <sub>4</sub>	22.331	-164.	2.273	0.04306
SiH <sub>4</sub>	22.240	-111.8	4.325	0.05791
CO	22.368	-191.5	1.454	0.03952
NO	22.362	-151.8	1.439	0.02887
CO <sub>2</sub>	22.252	-78.5 <sub>sublimes</sub>	3.610	0.04286
N <sub>2</sub> O	22.249	-88.5	3.803	0.04435
NO <sub>2</sub> (g)	...	21.2	5.294	0.04435
O <sub>3</sub>	22.274	-111.9	3.522	0.04871
SO <sub>2</sub>	22.066	-10.	6.776	0.05679
C <sub>2</sub> H <sub>6</sub>	22.171	-88.6	5.507	0.06513
C <sub>2</sub> H <sub>4</sub>	22.226	-103.7	4.552	0.05821
C <sub>2</sub> H <sub>2</sub>	22.212	-84.0	4.475	0.05241
C <sub>3</sub> H <sub>8</sub>	21.936	-42.1	9.267	0.09048

Source: B. E. Poling, J. M. Prausnitz, and J. P. O'Connell, *Properties of Gases and Liquids*, 5th ed. (New York: McGraw-Hill, 2000).

## Deviations from Charles' Law for Real Gases:



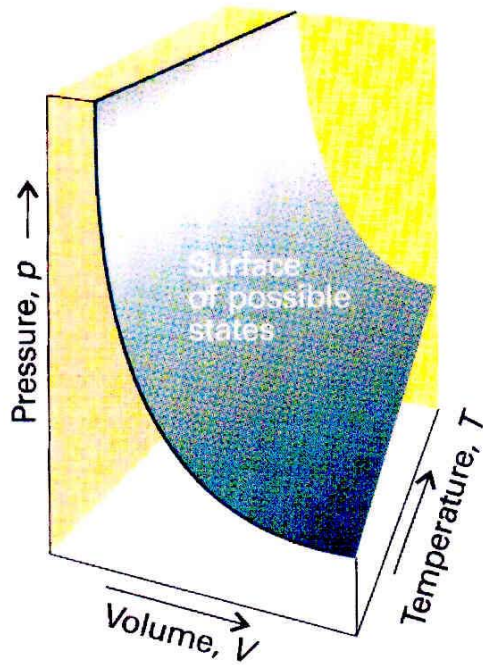
Copyright © 2006 Pearson Education, Inc., Publishing as Benjamin Cummings



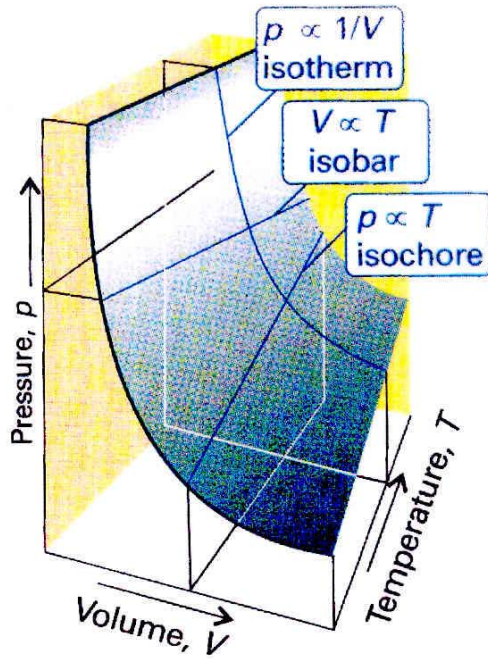
**1.15** The compression factor,  $Z$ , approaches 1 at low pressures, but does so with different slopes. For a perfect gas, the slope is zero, but real gases may have either positive or negative slopes, and the slope may vary with temperature. At the Boyle temperature, the slope is zero and the gas behaves perfectly over a wider range of conditions than at other temperatures.

At  $T < T_B$ , attractive forces predominate, and  $Z < 1$ .

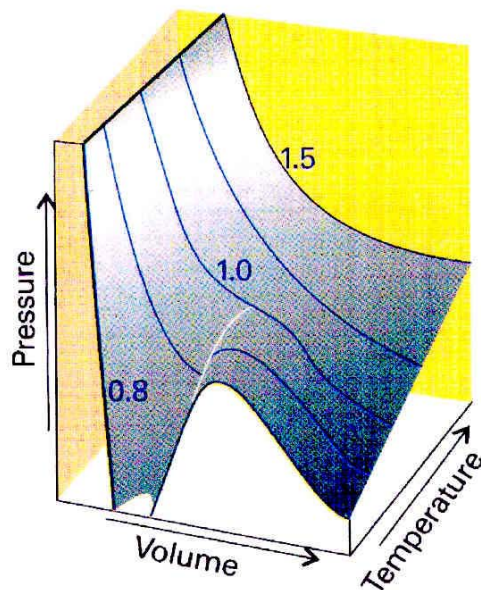
At  $T > T_B$ , repulsive forces predominate, and  $Z > 1$ .



**Fig. 1.8** A region of the  $p, V, T$  surface of a fixed amount of perfect gas. The points forming the surface represent the only states of the gas that can exist.



**Fig. 1.9** Sections through the surface shown in Fig. 1.8 at constant temperature give the isotherms shown in Fig. 1.4 and the isobars shown in Fig. 1.6.



**Fig. 1.17** The surface of possible states allowed by the van der Waals equation. Compare this surface with that shown in Fig. 1.8.

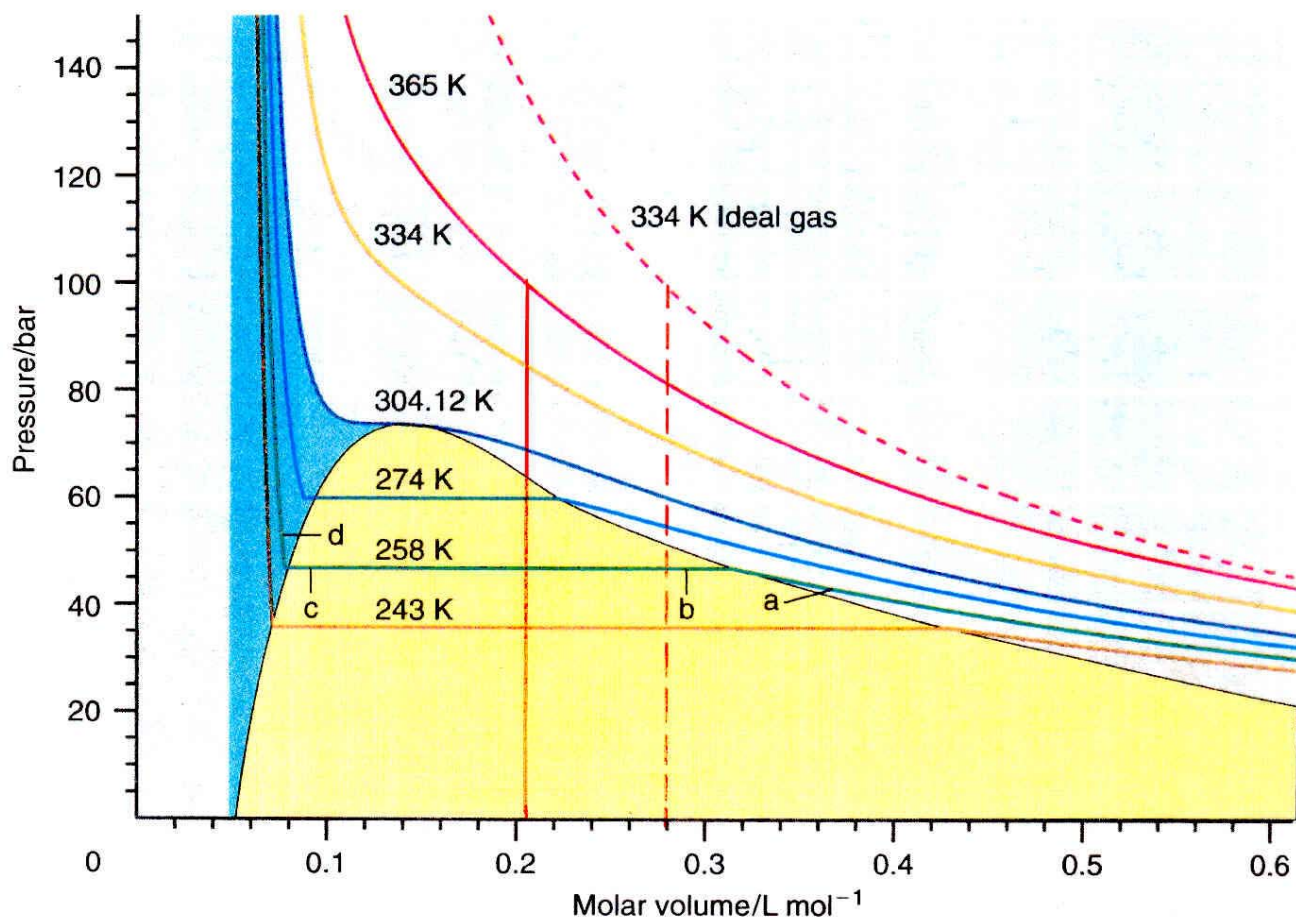


FIGURE 7.2

Calculated isotherms are shown for  $\text{CO}_2$ , modeled as a van der Waals gas. The gas and liquid (blue) regions, and the gas-liquid (yellow) coexistence region are shown. The dashed curve was calculated using the ideal gas law. The isotherm at  $T = 304.12 \text{ K}$  is at the critical temperature and is called the critical isotherm.

AT 258 K

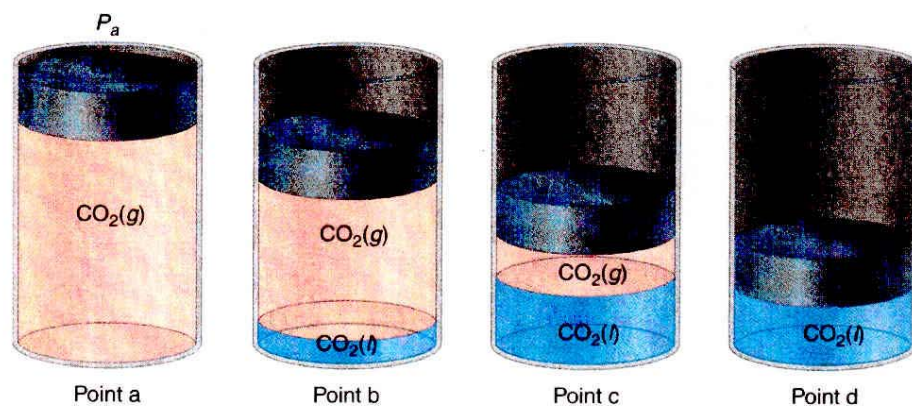


FIGURE 7.3

The volume and the composition of a system containing  $\text{CO}_2$  at  $258 \text{ K}$  are shown at the points a, b, c, and d indicated in Figure 7.2. The liquid and gas volumes are not shown to scale.