Statistical Molecular Thermodynamics

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Video 2.4

Law of Corresponding States

Critical Compressibility

TABLE 2.5
The experimental critical constants of various substances.

Species	T_c/K	P_c/bar	P_c/atm	$\overline{V}_c$/L·mol^{-1}	$P_c\overline{V}_c/RT_c$
Helium	5.1950	2.2750	2.2452	0.05780	0.30443
Neon	44.415	26.555	26.208	0.04170	0.29986
Argon	150.95	49.288	48.643	0.07530	0.29571
Krypton	210.55	56.618	55.878	0.09220	0.29819
Hydrogen	32.938	12.838	12.670	0.06500	0.30470
Carbon dioxide	304.14	73.843	72.877	0.09400	0.27443

$$\frac{P_c\overline{V}_c}{RT_c} = \frac{1}{R}\left(\frac{a}{27b^2}\right)(3b)\left(\frac{27bR}{8a}\right) = 0.375!$$

there is an apparent correspondence *between different "real" gases that is entirely independent of the van der Waals equation of state*

A Reduced Equation of State

$$\left(P + \frac{a}{\overline{V}^2}\right)\left(\overline{V} - b\right) = RT \qquad \overline{V}_c = 3b \qquad P_c = \frac{a}{27b^2} \qquad T_c = \frac{8a}{27bR}$$

$$\Downarrow$$

$$\left(P_R + \frac{3}{\overline{V}_R^2}\right)\left(\overline{V}_R - \frac{1}{3}\right) = \frac{8}{3}T_R \qquad P_R = \frac{P}{P_c} \qquad \overline{V}_R = \frac{\overline{V}}{\overline{V}_c} \qquad T_R = \frac{T}{T_c}$$

universal equation for *all* gases — reduced quantities

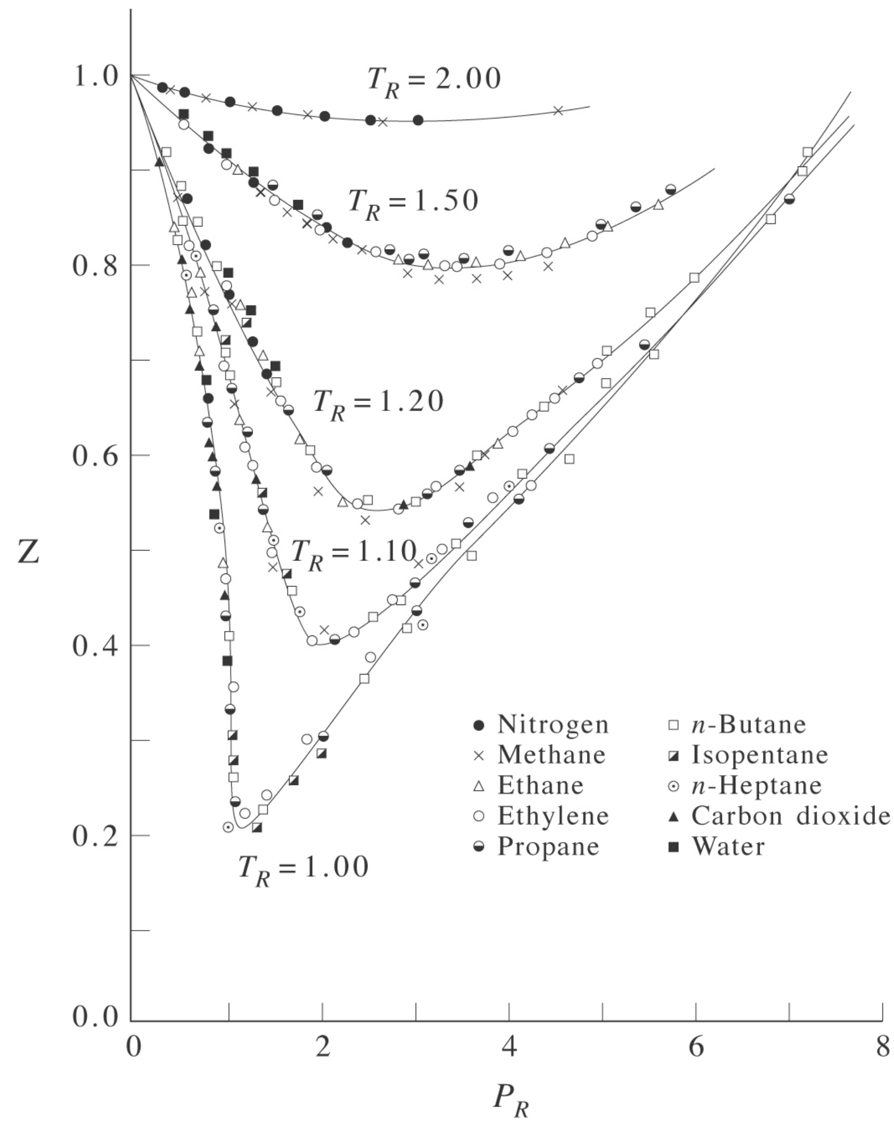
This is an example of the Law of Corresponding States: all gases have the same properties if compared at corresponding conditions.

Universal Compressibility Factor

$$Z = \frac{P\overline{V}}{RT}$$

$$= \frac{3\overline{V}_R}{3\overline{V}_R - 1} - \frac{9}{8\overline{V}_R T_R}$$

for vdW equation of state



Again, at "corresponding conditions" (relative to critical data), all gases behave equivalently.

Law of Corresponding States Example