Statistical Molecular Thermodynamics

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Video 2.1

Ideal Gas Equation of State

Gases Are the Simplest Phase

Their dilute character permits the study of relationships between temperature, pressure, and volume, that illustrate key principles of thermodynamics. The empirical study of gases revealed many apparent "laws".

Ideal Gas Equation of State

An *equation of state* details the mathematical relationship between the physical observables *pressure* (P), *volume* (V), and *temperature* (T)

The Ideal Gas obeys: $PV = nRT$ or $P\overline{V} = RT,\ \overline{V} = \frac{V}{n}$

universal gas constant (R) *molar volume* ($\overline{V}$)

Some definitions:

extensive variable
- depends on the size of the system (e.g., V, m (mass), E (energy))

intensive variable
- does *not* depend on the size of the system (e.g., T, P, ρ (density))

Observed Ideal Gas "Laws"

$$PV = nRT \quad \text{or} \quad P\overline{V} = RT,\ \overline{V} = \frac{V}{n}$$

At constant T, the product of P and $\overline{V}$ must be constant (Boyle's Law)

$$P_1\overline{V_1} = P_2\overline{V_2} \quad (\text{constant } T)$$

At constant P, the ratio of $\overline{V}$ and T must be constant (Charles' Law)

$$\frac{\overline{V_1}}{T_1} = \frac{\overline{V_2}}{T_2} \quad (\text{constant } P)$$

At constant V,n the ratio of P and T must be constant (Amonton's Law)

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad (\text{constant } V,n)$$

At constant P,T the ratio of V and n must be constant (Avogadro's Law)

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \quad (\text{constant } P,T)$$

Temperature and the Gas Constant

Operational definition of temperature: $T = \lim_{P \to 0} \frac{P\overline{V}}{R}$

Using Amonton's law, can extrapolate P vs T for a sealed, fixed volume to $P = 0$ in order to define $T = 0$

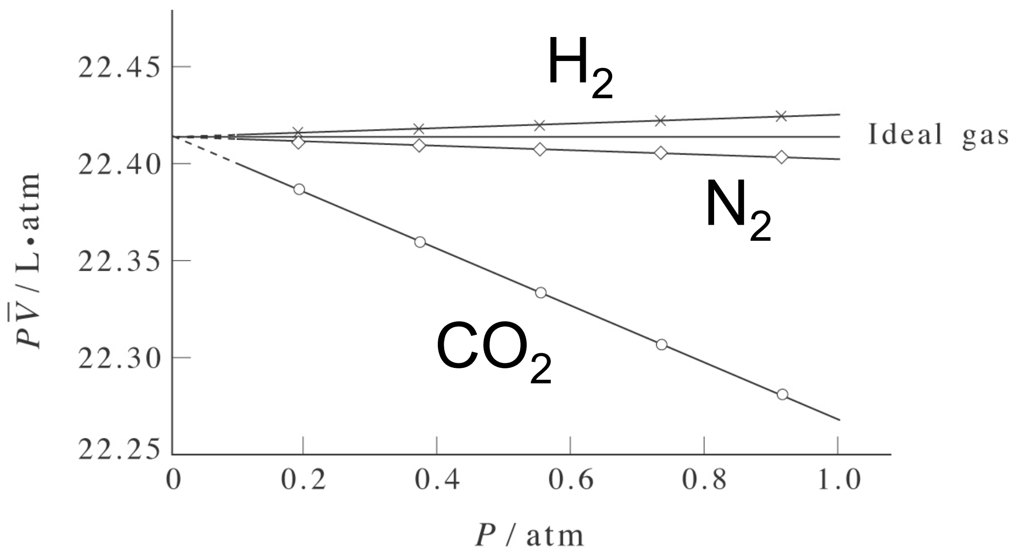
Another fixed temperature, the triple point of water, is taken to be 273.16 K, which permits assignment of R

$$T / °C = T / K - 273.15$$

273.15 *K* measurements

At low pressures, *all* gases converge to ideal behavior

$$P\overline{V}(273.15) = 22.414 \text{ L} \bullet \text{atm} \bullet \text{mol}^{-1}$$

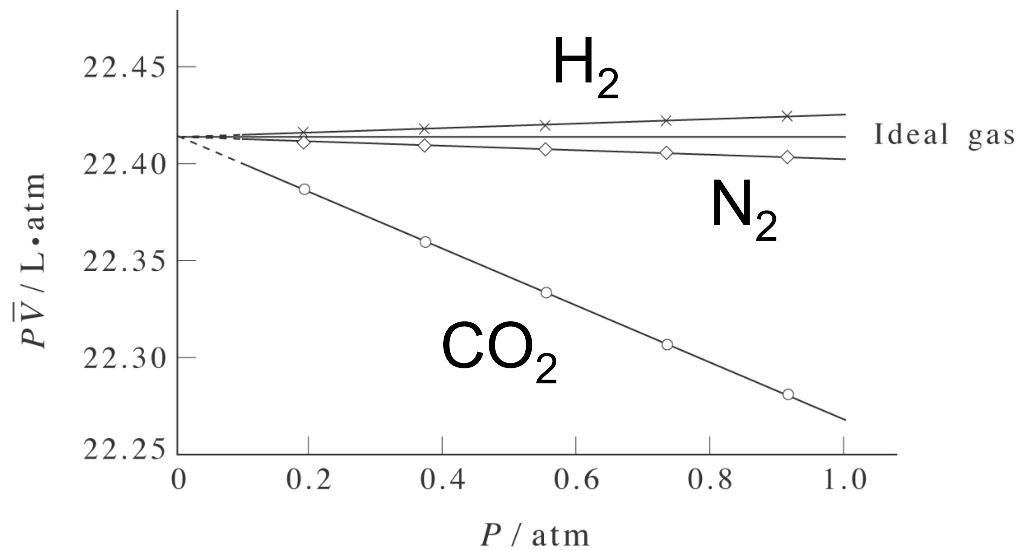


TEMPERATURE AND THE GAS CONSTANT

Determination of universal gas constant: $R = \lim_{P \to 0} \frac{P\overline{V}}{T}$

0.082058 L•atm•mol^{-1}•K^{-1}
0.083145 L•bar•mol^{-1}•K^{-1}
83.145 cm^3•bar•mol^{-1}•K^{-1}
8.3145 J•mol^{-1}•K^{-1}

273.15 *K* measurements



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