

Physical Chemistry Laboratory, I
CHEM 445
Experiment 5
Heat Capacity Ratio for Gases
 (Revised, 1/10/03)

The heat capacity for a substance is the amount of heat needed to raise the temperature of the substance by 1 °C or 1 K. The heat capacities depend on the chemical nature of the substance, on the physical state of the substance, on the temperature, and on whether P or V is held constant during the process: C_P or C_V .

For liquids and solids, $C_V = C_P$ and the two terms are often used interchangeably. However, for ideal gases, it is well known (Tinoco, Jr., Sauer, and Wang or Noggle) that

$$\bar{C}_P = \bar{C}_V + R \quad (1)$$

In this equation, $\bar{C}$ = molar heat capacity of the gas, either at constant pressure or at constant volume. The bar over a symbol refers to that quantity per mol of substance. The molar heat capacities are defined by the equations,

$$\bar{C}_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V \quad \text{and} \quad \bar{C}_P = \left(\frac{\partial \bar{H}}{\partial T} \right)_P \quad (2)$$

For a monatomic gas, there is no rotational or vibrational energy and if the temperature is relatively low, only the ground electronic state of the species is populated to any extent. Consequently, only translational energy is involved; and from kinetic theory,

$$\bar{C}_V = \frac{3R}{2} \quad \text{and} \quad \bar{C}_P = \frac{5R}{2} \quad (3)$$

For polyatomic gases, there are additional forms of energy that contribute to the heat capacity.

$$E = E(\text{trans}) + E(\text{rot}) + E(\text{vib}) \quad (4)$$

For many simple diatomic molecules, however, the vibrational contribution to the heat capacity is small, and in the neighborhood of room temperature, $C_V = \frac{5R}{2}$. However, the heat capacities of diatomic molecules increase with increasing temperature as the vibrational modes become active.

The heat capacities of polyatomic molecules are more complex and less predictable. The equipartition principle predicts that the heat capacity depends on the number of vibrational degrees of freedom in the molecule that is determined by the number of atoms in the molecule. The equipartition model is incorrect in its predictions but is useful because it does indicate that the heat capacity will increase with increasing molecular complexity (number of atoms or number of bonds).

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