

7.2: Internal Pressure

The partial derivative $(\partial U/\partial V)_T$ applied to a fluid phase in a closed system is called the **internal pressure**. (Note that U and pV have dimensions of energy; therefore, U/V has dimensions of pressure.)

To relate the internal pressure to other properties, we divide Eq. 5.2.2 by dV : $dU/dV = T(dS/dV) - p$. Then we impose a condition of constant T : $(\partial U/\partial V)_T = T(\partial S/\partial V)_T - p$. When we make a substitution for $(\partial S/\partial V)_T$ from the Maxwell relation of Eq. 5.4.17, we obtain

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \quad (7.2.1)$$

(closed system,
fluid phase, $C=1$)

This equation is sometimes called the “thermodynamic equation of state” of the fluid.

For an ideal-gas phase, we can write $p = nRT/V$ and then

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V} = \frac{p}{T} \quad (7.2.2)$$

Making this substitution in Eq. 7.2.1 gives us

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad (7.2.3)$$

(closed system of an ideal gas)

showing that the internal pressure of an ideal gas is zero.

In Sec. 3.5.1, an ideal gas was defined as a gas (1) that obeys the ideal gas equation, and (2) for which U in a closed system depends only on T . Equation 7.2.3, derived from the first part of this definition, expresses the second part. It thus appears that the second part of the definition is redundant, and that we could define an ideal gas simply as a gas obeying the ideal gas equation. This argument is valid only if we assume the ideal-gas temperature is the same as the thermodynamic temperature (Secs. 2.3.5 and 4.3.4) since this assumption is required to derive Eq. 7.2.3.

Without this assumption, we can't define an ideal gas solely by $pV = nRT$, where T is the ideal gas temperature.

Here is a simplified interpretation of the significance of the internal pressure. When the volume of a fluid increases, the average distance between molecules increases and the potential energy due to intermolecular forces changes. If attractive forces dominate, as they usually do unless the fluid is highly compressed, expansion causes the potential energy to *increase*. The internal energy is the sum of the potential energy and thermal energy. The internal pressure, $(\partial U/\partial V)_T$, is the rate at which the internal energy changes with volume at constant temperature. At constant temperature, the thermal energy is constant so that the internal pressure is the rate at which just the potential energy changes with volume. Thus, the internal pressure is a measure of the strength of the intermolecular forces and is positive if attractive forces dominate. (These attractive intermolecular forces are the cohesive forces that can allow a negative pressure to exist in a liquid; see Sec. 2.3.4.) In an ideal gas, intermolecular forces are absent and therefore the internal pressure of an ideal gas is zero.

With the substitution $(\partial p/\partial T)_V = \alpha/\kappa_T$ (Eq. 7.1.7), Eq. 7.2.1 becomes

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{\alpha T}{\kappa_T} - p \quad (7.2.4)$$

(closed system,
fluid phase, $C=1$)

The internal pressure of a liquid at $p = 1$ bar is typically much larger than 1 bar (see Prob. 7.6). Equation 7.2.4 shows that, in this situation, the internal pressure is approximately equal to $\alpha T/\kappa_T$.

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