

7.6: Isothermal Pressure Changes

In various applications, we will need expressions for the effect of changing the pressure at constant temperature on the internal energy, enthalpy, entropy, and Gibbs energy of a phase. We obtain the expressions by integrating expressions found in Table 7.1. For example, ΔU is given by $\int (\partial U / \partial p)_T dp$. The results are listed in the second column of Table 7.4.

7.6.1 Ideal gases

Simplifications result when the phase is an ideal gas. In this case, we can make the substitutions $V = nRT/p$, $\alpha = 1/T$, and $\kappa_T = 1/p$, resulting in the expressions in the third column of Table 7.4.

The expressions in the third column of Table 7.4 may be summarized by the statement that, when an ideal gas expands isothermally, the internal energy and enthalpy stay constant, the entropy increases, and the Helmholtz energy and Gibbs energy decrease.

7.6.2 Condensed phases

Solids, and liquids under conditions of temperature and pressure not close to the critical point, are much less compressible than gases. Typically the isothermal compressibility, κ_T , of a liquid or solid at room temperature and atmospheric pressure is no greater than $1 \times 10^{-4} \text{ bar}^{-1}$ (see Fig. 7.2), whereas an ideal gas under these conditions has $\kappa_T = 1/p = 1 \text{ bar}^{-1}$. Consequently, it is frequently valid to treat V for a liquid or solid as essentially constant during a pressure change at constant temperature. Because κ_T is small, the product $\kappa_T p$ for a liquid or solid is usually much smaller than the product αT . Furthermore, κ_T for liquids and solids does not change rapidly with p as it does for gases, and neither does α .

With the approximations that V , α , and κ_T are constant during an isothermal pressure change, and that $\kappa_T p$ is negligible compared with αT , we obtain the expressions in the last column of Table 7.4.

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