

8.3: How Enthalpy Depends on Pressure

Let us look briefly at the approximations $\Delta H (\text{B}^* \rightarrow \text{C}) \approx 0$ and $\Delta H (\text{D}^* \rightarrow \text{A}) \approx 0$ that we used in [Section 8.2](#). In these steps, the pressure changes while the temperature remains constant. In [Chapter 10](#), we find a general relationship for the pressure-dependence of a system's enthalpy:

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

This evaluates to zero for an ideal gas and to a negligible quantity for many other systems.

For liquids and solids, information on the variation of volume with temperature is collected in tables as the **coefficient of thermal expansion**, α , where

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

Consequently, the dependence of enthalpy on pressure is given by

$$\left(\frac{\partial H}{\partial P}\right)_T = V(1 - \alpha T)$$

For ice, $\alpha \approx 50 \times 10^{-6} \text{ K}^{-1}$ and the molar volume near 0 C is $19.65 \text{ cm}^3 \text{ mol}^{-1}$. The enthalpy change for compressing one mole of ice from the sublimation pressure to 1 atm is $\Delta H (\text{D}^* \rightarrow \text{A}) = 2 \text{ J mol}^{-1}$.

To find the enthalpy change for expanding one mole of water vapor at 100 C from 1 atm to the sublimation pressure, we use the virial equation and tabulated coefficients for water vapor to calculate $(\partial H / \partial P)_{398 \text{ K}}$. We find $\Delta H (\text{B}^* \rightarrow \text{C}) = 220 \text{ J mol}^{-1}$. (See problem 9.)

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