

4.6: Useful Definitions and Relationships

In this chapter (and in the previous chapter), several useful definitions have been stated.

Toolbox of useful Relationships

The following “measurable quantities” have been defined:

- **Heat Capacities:**

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_V$$

and

$$C_p \equiv \left(\frac{\partial H}{\partial T} \right)_p$$

- **Coefficient of Thermal Expansion:**

$$\alpha \equiv \left(\frac{\partial V}{\partial T} \right)_p$$

or

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

- **Isothermal Compressibility:**

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

or

$$\left(\frac{\partial V}{\partial p} \right)_T = -V\kappa_T$$

The following relation has been derived:

$$\frac{\alpha}{\kappa_T} = \left(\frac{\partial p}{\partial T} \right)_V$$

And the following relationships were given without proof (yet!):

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

and

$$\left(\frac{\partial H}{\partial p} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_p - p$$

Together, these relationships and definitions make a powerful set of tools that can be used to derive a number of very useful expressions.

Example 4.6.1: Expanding Thermodynamic Function

Derive an expression for $\left(\frac{\partial H}{\partial V} \right)_T$ in terms of measurable quantities.

Solution 1:

Begin by using the total differential of $H(p, T)$:

$$dH = \left(\frac{\partial H}{\partial p} \right)_T dp + \left(\frac{\partial H}{\partial T} \right)_p dT$$

Divide by dV and constrain to constant T (to generate the partial of interest on the left):

$$\left. \frac{dH}{dV} \right|_T = \left(\frac{\partial H}{\partial p} \right)_T \left. \frac{dp}{dV} \right|_T + \left(\frac{\partial H}{\partial T} \right)_p \left. \frac{dT}{dV} \right|_T$$

The last term on the right will vanish (since $dT = 0$ for constant T). After converting to partial derivatives

$$\left(\frac{\partial H}{\partial V} \right)_T = \left(\frac{\partial H}{\partial p} \right)_T \left(\frac{\partial p}{\partial V} \right)_T \quad (4.6.1)$$

This result is simply a demonstration of the “chain rule” on partial derivatives! But now we are getting somewhere. We can now substitute for $\left(\frac{\partial H}{\partial V} \right)_T$ using our “toolbox of useful relationships”:

$$\left(\frac{\partial H}{\partial V} \right)_T = \left[-T \left(\frac{\partial V}{\partial T} \right)_p + V \right] \left(\frac{\partial p}{\partial V} \right)_T$$

Using the distributive property of multiplication, this expression becomes

$$\left(\frac{\partial H}{\partial V} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial V} \right)_T + V \left(\frac{\partial p}{\partial V} \right)_T \quad (4.6.2)$$

Using the cyclic permutation rule (Transformation Type II), the middle term of Equation 4.6.2 can be simplified

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cyclic permutation rule? Where is that on the Libraries?

$$\left(\frac{\partial H}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V + V \left(\frac{\partial p}{\partial V} \right)_T$$

And now all of the partial derivatives on the right can be expressed in terms of α and κ_T (along with T and V , which are also “measurable properties”).

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

or

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

✓ Example 4.6.2: Isothermal Compression

Calculate ΔH for the isothermal compression of ethanol which will decrease the molar volume by 0.010 L/mol at 300 K . (For ethanol, $\alpha = 1.1 \times 10^{-3} \text{ K}^{-1}$ and $\kappa_T = 7.9 \times 10^{-5} \text{ atm}^{-1}$).

Solution

Integrating the total differential of H at constant temperature results in

$$\Delta H = \left(\frac{\partial H}{\partial V} \right)_T \Delta V$$

From Example 4.6.1, we know that

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

so

$$\Delta H = \left[\frac{1}{7.9 \times 10^{-5} \text{ atm}^{-1}} ((300 \text{ K})(1.1 \times 10^{-3} \text{ K}^{-1}) - 1) \right] (-0.010 \text{ L/mol})$$

$$\Delta H = \left(84.81 \frac{\text{atm}\cancel{\text{L}}}{\text{mol}} \right) \underbrace{\left(\frac{8.314 \text{ J}}{0.8206 \text{ atm}\cancel{\text{L}}} \right)}_{\text{conversion factor}} = 9590 \text{ J/mol}$$

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