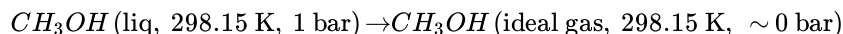


8.5: The Ideal Gas Standard State

The ideal gas standard state is a useful invention, which has additional advantages that emerge as our development proceeds. For permanent gases—gases whose behavior is approximately ideal anyway—there is a negligible difference between the enthalpy in the ideal gas state and the enthalpy at 1 bar.

For volatile substances that are normally liquid or solid at 1 bar, the ideal gas standard state becomes a second standard state. For such substances, data tables frequently give the standard enthalpy of formation for both the condensed phase (designated $\Delta_f H^\circ(\text{liq})$ or $\Delta_f H^\circ(\text{s})$) and the ideal gas standard state (designated $\Delta_f H^\circ(\text{g})$). For example, the CODATA¹ values for the standard enthalpies of formation for liquid and ideal-gas methanol are -239.2 and $-201.0 \text{ kJ mol}^{-1}$, respectively, at 298.15 K. The difference between these values is the enthalpy change in vaporizing one mole of liquid methanol to its ideal gas standard state at 298.15 K:



Since this is the difference between the enthalpy of methanol in its standard state as an ideal gas and methanol in its standard state as a liquid, we can call this difference the standard enthalpy of vaporization for methanol:

$$\Delta_{\text{vap}} H^\circ = \Delta_f H^\circ(\text{g}, 298.15 \text{ K}, \sim 0 \text{ bar}) - \Delta_f H^\circ(\text{g}, 298.15 \text{ K}, 1 \text{ bar}) = 37.40 \text{ kJ mol}^{-1}$$

This is not a reversible process, because liquid methanol at 1 bar is not at equilibrium with its vapor at an arbitrarily low pressure at 298.15 K.

Note that $\Delta_{\text{vap}} H^\circ$ is not the same as the ordinary enthalpy of vaporization, $\Delta_{\text{vap}} H$. The ordinary enthalpy of vaporization is the enthalpy change for the reversible vaporization of liquid methanol to real methanol vapor at a pressure of 1 atm and the normal boiling temperature. We write it without the superscript degree sign because methanol vapor is not produced in its standard state. For methanol, the normal boiling point and enthalpy of vaporization² are 337.8 K and $35.21 \text{ kJ mol}^{-1}$, respectively.

We can devise a cycle that relates these two vaporization processes to one another: Summing the steps below yields the process for vaporizing liquid methanol in its standard state to methanol vapor in its standard state.

1. $\text{CH}_3\text{OH}(\text{liq}, 298.15 \text{ K}, 1 \text{ bar}) \rightarrow \text{CH}_3\text{OH}(\text{liq}, 337.8 \text{ K}, 1 \text{ bar}) \Delta_{(1)} H$
2. $\text{CH}_3\text{OH}(\text{liq}, 337.8 \text{ K}, 1 \text{ bar}) \rightarrow \text{CH}_3\text{OH}(\text{liq}, 337.8 \text{ K}, 1 \text{ atm}) \Delta_{(2)} H$
3. $\text{CH}_3\text{OH}(\text{liq}, 337.8 \text{ K}, 1 \text{ atm}) \rightarrow \text{CH}_3\text{OH}(\text{g}, 337.8 \text{ K}, 1 \text{ atm})$

$$\Delta_{(3)} H = \Delta_{\text{vap}} H$$

4. $\text{CH}_3\text{OH}(\text{g}, 337.8 \text{ K}, 1 \text{ atm}) \rightarrow \text{CH}_3\text{OH}(\text{g}, 337.8 \text{ K}, \sim 0 \text{ bar}) \Delta_{(4)} H$
5. $\text{CH}_3\text{OH}(\text{g}, 337.8 \text{ K}, \sim 0 \text{ bar}) \rightarrow \text{CH}_3\text{OH}(\text{g}, 298.15 \text{ K}, \sim 0 \text{ bar}) \Delta_{(5)} H$

Thus, we have

$$\Delta_{\text{vap}} H^\circ = \Delta_{(1)} H + \Delta_{(2)} H + \Delta_{\text{vap}} H + \Delta_{(4)} H + \Delta_{(5)} H$$

$\Delta_{(1)} H$ and $\Delta_{(5)} H$ can be evaluated by integrating the heat capacities for the liquid and gas, respectively. $\Delta_{(2)} H$ and $\Delta_{(4)} H$ can be evaluated by integrating $(\partial H / \partial P)_T$ for the liquid and gas, respectively. $\Delta_{(3)} H$ is negligible. (For the evaluation of these quantities, see problem 10.)

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