

8.3: Phase Transitions

Recall (Sec. 2.2.2) that an equilibrium phase transition of a pure substance is a process in which some or all of the substance is transferred from one coexisting phase to another at constant temperature and pressure.

8.3.1 Molar transition quantities

The quantity $\Delta_{\text{vap}}H$ is the molar enthalpy change for the reversible process in which liquid changes to gas *at a temperature and pressure at which the two phases coexist at equilibrium*. This quantity is called the **molar enthalpy of vaporization**. (Because $\Delta_{\text{vap}}H$ is an enthalpy *change* per amount of vaporization, it would be more accurate to call it the “molar enthalpy change of vaporization.”) Since the pressure is constant during the process, $\Delta_{\text{vap}}H$ is equal to the heat per amount of vaporization (Eq. 5.3.8). Hence, $\Delta_{\text{vap}}H$ is also called the **molar heat of vaporization**.

The IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition, RSC Publishing, Cambridge, 2007, p. 58) recommends that Δ_p be interpreted as an operator symbol: $\Delta_p \stackrel{\text{def}}{=} \partial/\partial\xi_p$, where “p” is the abbreviation for a process at constant T and p (in this case “vap”) and ξ_p is its advancement. Thus $\Delta_{\text{vap}}H$ is the same as $(\partial H/\partial\xi_{\text{vap}})_{T,p}$ where ξ_{vap} is the amount of liquid changed to gas.

Here is a list of symbols for the molar enthalpy changes of various equilibrium phase transitions:

$$\begin{aligned}\Delta_{\text{vap}}H & \text{ molar enthalpy of vaporization (liquid} \rightarrow \text{gas)} \\ \Delta_{\text{sub}}H & \text{ molar enthalpy of sublimation (solid} \rightarrow \text{gas)} \\ \Delta_{\text{fus}}H & \text{ molar enthalpy of fusion (solid} \rightarrow \text{liquid)} \\ \Delta_{\text{trs}}H & \text{ molar enthalpy of a transition between any two phases in general}\end{aligned}\tag{8.3.1}$$

Molar enthalpies of vaporization, sublimation, and fusion are *positive*. The reverse processes of condensation (gas \rightarrow liquid), condensation or deposition (gas \rightarrow solid), and freezing (liquid \rightarrow solid) have *negative* enthalpy changes.

The subscripts in the list above are also used for other molar transition quantities. Thus, there is the molar entropy of vaporization $\Delta_{\text{vap}}S$, the molar internal energy of sublimation $\Delta_{\text{sub}}U$, and so on.

A molar transition quantity of a pure substance is the change of an extensive property divided by the amount transferred between the phases. For example, when an amount n in a liquid phase is allowed to vaporize to gas at constant T and p , the enthalpy change is $\Delta H = nH_{\text{m}}^{\text{g}} - nH_{\text{m}}^{\text{l}}$ and the molar enthalpy of vaporization is

$$\Delta_{\text{vap}}H = \frac{\Delta H}{n} = H_{\text{m}}^{\text{g}} - H_{\text{m}}^{\text{l}}\tag{8.3.1}$$

(pure substance)

In other words, $\Delta_{\text{vap}}H$ is the enthalpy change per amount vaporized and is also the difference between the molar enthalpies of the two phases.

A molar property of a phase, being intensive, usually depends on two independent intensive variables such as T and p . Despite the fact that $\Delta_{\text{vap}}H$ is the difference of the two molar properties H_{m}^{g} and H_{m}^{l} , its value depends on only *one* intensive variable, because the two phases are in transfer equilibrium and the system is univariant. Thus, we may treat $\Delta_{\text{vap}}H$ as a function of T only. The same is true of any other molar transition quantity.

The molar Gibbs energy of an equilibrium phase transition, $\Delta_{\text{trs}}G$, is a special case. For the phase transition $\alpha \rightarrow \beta$, we may write an equation analogous to Eq. 8.3.1 and equate the molar Gibbs energy in each phase to a chemical potential (see Eq. 7.8.1):

$$\Delta_{\text{trs}}G = G_{\text{m}}^{\beta} - G_{\text{m}}^{\alpha} = \mu^{\beta} - \mu^{\alpha}\tag{8.3.2}$$

(pure substance)

But the transition is between two phases at equilibrium, requiring both phases to have the same chemical potential: $\mu^{\beta} - \mu^{\alpha} = 0$. Therefore, the molar Gibbs energy of *any* equilibrium phase transition is zero:

$$\Delta_{\text{trs}}G = 0\tag{8.3.3}$$

(pure substance)

Since the Gibbs energy is defined by $G = H - TS$, in phase α we have $G_{\text{m}}^{\alpha} = G^{\alpha}/n^{\alpha} = H_{\text{m}}^{\alpha} - TS_{\text{m}}^{\alpha}$. Similarly, in phase β we have $G_{\text{m}}^{\beta} = H_{\text{m}}^{\beta} - TS_{\text{m}}^{\beta}$. When we substitute these expressions in $\Delta_{\text{trs}}G = G_{\text{m}}^{\beta} - G_{\text{m}}^{\alpha}$ (Eq. 8.3.2) and set T equal to the transition

temperature T_{trs} , we obtain

$$\Delta_{\text{trs}}G = (H_{\text{m}}^{\beta} - H_{\text{m}}^{\alpha}) - T_{\text{trs}}(S_{\text{m}}^{\beta} - S_{\text{m}}^{\alpha}) = \Delta_{\text{trs}}H - T_{\text{trs}}\Delta_{\text{trs}}S \quad (8.3.4)$$

Then, by setting $\Delta_{\text{trs}}G$ equal to zero, we find the molar entropy and molar enthalpy of the equilibrium phase transition are related by

$$\Delta_{\text{trs}}S = \frac{\Delta_{\text{trs}}H}{T_{\text{trs}}} \quad (8.3.5)$$

(pure substance)

where $\Delta_{\text{trs}}S$ and $\Delta_{\text{trs}}H$ are evaluated at the transition temperature T_{trs} .

We may obtain Eq. 8.3.5 directly from the second law. With the phases in equilibrium, the transition process is reversible. The second law gives $\Delta S = q/T_{\text{trs}} = \Delta H/T_{\text{trs}}$. Dividing by the amount transferred between the phases gives Eq. 8.3.5.

8.3.2 Calorimetric measurement of transition enthalpies

The most precise measurement of the molar enthalpy of an equilibrium phase transition uses electrical work. A known quantity of electrical work is performed on a system containing coexisting phases, in a constant-pressure adiabatic calorimeter, and the resulting amount of substance transferred between the phases is measured. The first law shows that the electrical work $I^2 R_{\text{el}} \Delta t$ equals the heat that would be needed to cause the same change of state. This heat, at constant p , is the enthalpy change of the process.

The method is similar to that used to measure the heat capacity of a phase at constant pressure (Sec. 7.3.2), except that now the temperature remains constant and there is no need to make a correction for the heat capacity of the calorimeter.

8.3.3 Standard molar transition quantities

The *standard* molar enthalpy of vaporization, $\Delta_{\text{vap}}H^{\circ}$, is the enthalpy change when pure liquid in its standard state at a specified temperature changes to gas in its standard state at the same temperature, divided by the amount changed.

Note that the initial state of this process is a real one (the pure liquid at pressure p°), but the final state (the gas behaving ideally at pressure p°) is hypothetical. The liquid and gas are not necessarily in equilibrium with one another at pressure p° and the temperature of interest, and we cannot evaluate $\Delta_{\text{vap}}H^{\circ}$ from a calorimetric measurement with electrical work without further corrections. The same difficulty applies to the evaluation of $\Delta_{\text{sub}}H^{\circ}$. In contrast, $\Delta_{\text{vap}}H$ and $\Delta_{\text{sub}}H$ (without the $^{\circ}$ symbol), as well as $\Delta_{\text{fus}}H^{\circ}$, all refer to reversible transitions between two *real* phases coexisting in equilibrium.

Let X represent one of the thermodynamic potentials or the entropy of a phase. The standard molar transition quantities $\Delta_{\text{vap}}X^{\circ} = X_{\text{m}}^{\circ}(\text{g}) - X_{\text{m}}(\text{l})$ and $\Delta_{\text{sub}}X^{\circ} = X_{\text{m}}^{\circ}(\text{g}) - X_{\text{m}}(\text{s})$ are functions only of T . To evaluate $\Delta_{\text{vap}}X^{\circ}$ or $\Delta_{\text{sub}}X^{\circ}$ at a given temperature, we must calculate the change of X_{m} for a path that connects the standard state of the liquid or solid with that of the gas. The simplest choice of path is one of constant temperature T with the following steps:

1. The sum of ΔX_{m} for these three steps is the desired quantity $\Delta_{\text{vap}}X^{\circ}$ or $\Delta_{\text{sub}}X^{\circ}$.

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