7.4: Heating at Constant Volume or Pressure

Consider the process of changing the temperature of a phase at constant volume.

> Keeping the volume exactly constant while increasing the temperature is not as simple as it may sound. Most solids expand when heated, unless we arrange to increase the external pressure at the same time. If we use solid walls to contain a fluid phase, the container volume will change with temperature. For practical purposes, these volume changes are usually negligible.

The rate of change of internal energy with T at constant V is the heat capacity at constant volume: $C_V = (\partial U/\partial T)_V$ (Eq. 7.3.1). Accordingly, an infinitesimal change of U is given by

$$\mathrm{d}U = C_V \, \mathrm{d}T \tag{7.4.1}$$
$$\text{(closed system,}$$
$$C{=}1,\, P{=}1,\, \text{constant } V)$$

and the finite change of U between temperatures T_1 and T_2 is

$$\Delta U = \int_{T_1}^{T_2} C_V \, \mathrm{d}T \tag{7.4.2}$$
$$\text{(closed system,}$$
$$C{=}1,\, P{=}1,\, \text{constant } V)$$

Three comments, relevant to these and other equations in this chapter, are in order:

1.
2. If, at a fixed volume and over the temperature range T_1 to T_2, the value of C_V is essentially constant (i.e., independent of T), Eq. 7.4.2 becomes

$$\Delta U = C_V (T_2 - T_1) \tag{7.4.5}$$
$$\text{(closed system, } C{=}1,$$
$$P{=}1,\, \text{constant } V \text{ and } C_V)$$

An infinitesimal entropy change during a reversible process in a closed system is given according to the second law by $\mathrm{d}S = đq/T$. At constant volume, $đq$ is equal to $\mathrm{d}U$ which in turn equals $C_V \, \mathrm{d}T$. Therefore, the entropy change is

$$\mathrm{d}S = \frac{C_V}{T} \, \mathrm{d}T \tag{7.4.6}$$
$$\text{(closed system,}$$
$$C{=}1,\, P{=}1,\, \text{constant } V)$$

Integration yields the finite change

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V}{T} \, \mathrm{d}T \tag{7.4.7}$$
$$\text{(closed system,}$$
$$C{=}1,\, P{=}1,\, \text{constant } V)$$

If C_V is treated as constant, Eq. 7.4.7 becomes

$$\Delta S = C_V \ln \frac{T_2}{T_1} \tag{7.4.8}$$
$$\text{(closed system, } C{=}1,$$
$$P{=}1,\, \text{constant } V \text{ and } C_V)$$

(More general versions of the two preceding equations have already been given in Sec. 4.6.1.)

We may derive relations for a temperature change at constant *pressure* by the same methods. From $C_p = (\partial H/\partial T)_p$ (Eq. 7.3.2), we obtain

$$\Delta H = \int_{T_1}^{T_2} C_p \, \mathrm{d}T \tag{7.4.9}$$
$$\text{(closed system,}$$
$$C{=}1,\, P{=}1,\, \text{constant } p)$$

If C_p is treated as constant, Eq. 7.4.9 becomes

$$\Delta H = C_p(T_2 - T_1)$$

$$(7.4.10)$$
$$\text{(closed system, } C=1,$$
$$P=1, \text{ constant } p \text{ and } C_p)$$

From $\mathrm{d}S = đq/T$ and Eq. 7.3.2 we obtain for the entropy change at constant pressure

$$\mathrm{d}S = \frac{C_p}{T}\,\mathrm{d}T$$

$$(7.4.11)$$
$$\text{(closed system,}$$
$$C=1, P=1, \text{ constant } p)$$

Integration gives

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T}\,\mathrm{d}T$$

$$(7.4.12)$$
$$\text{(closed system,}$$
$$C=1, P=1, \text{ constant } p)$$

or, with C_p treated as constant,

$$\Delta S = C_p \ln \frac{T_2}{T_1}$$

$$(7.4.13)$$
$$\text{(closed system, } C=1,$$
$$P=1, \text{ constant } p \text{ and } C_p)$$

C_p is positive, so heating a phase at constant pressure causes H and S to increase.

The Gibbs energy changes according to $(\partial G/\partial T)_p = -S$ (Eq. 5.4.11), so heating at constant pressure causes G to decrease.