1. **Heat Capacity:**
   Heat capacity is defined as the change in temperature of a system with a change of heat transferred to the system:

$$C \equiv \frac{dQ}{dT}$$

C= heat capacity
Q= heat
T= Temperature

Heat Capacity at Constant Volume
The constant-volume heat capacity is defined as:

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V \qquad (2.16)$$

This definition accommodates both the molar heat capacity and the specific heat capacity (usually called specific heat), depending on whether U is the molar or specific internal energy.

Specific heat capacity: the amount of heat needed to raise the temperature of a unit mass of material by one degree.

Eq. (2.16) may be written for a constant-volume process in a closed system as

$$dU = C_V\, dT \qquad \text{(const V)} \qquad (2.17)$$

Integration yields:

$$\Delta U = \int_{T_1}^{T_2} C_V\, dT \qquad (\text{const } V) \qquad (2.18)$$

The combination of this result with Eq. (2.10) for a mechanically reversible, constant-volume process gives:

$$Q = n\, \Delta U = n \int_{T_1}^{T_2} C_V\, dT \qquad (\text{const } V) \qquad (2.19)$$

If the volume varies during the process but returns at the end of the process to its initial value, the process cannot rightly be called one of constant volume, even though $V_2 = V_1$ and $\Delta V = 0$

Heat Capacity at Constant Pressure

The constant-pressure heat capacity is defined as:

$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P \qquad (2.20)$$

Eq. (2.20) is equally well written for a constant-pressure, closed-system process as:

$$dH = C_P\, dT \qquad \text{(const } P\text{)} \qquad (2.21)$$

$$\Delta H = \int_{T_1}^{T_2} C_P\, dT \qquad \text{(const } P\text{)} \qquad (2.22)$$

For a mechanically reversible, constant-pressure process, this result may be combined with Eq. (2.13) to give

$$Q = n\ AH = n \int_{T_1}^{T_2} C_P\, dT \qquad \text{(const } P\text{)} \qquad (2.23)$$

Example 2.9

Air at 1 bar and 298.15 K (25°C) is compressed to 5 bar and 298.15 K by two different mechanically reversible processes:

(*a*) Cooling at constant pressure followed by heating at constant volume.

(*b*) Heating at constant volume followed by cooling at constant pressure.

Calculate the heat and work requirements and ΔU and ΔH of the air for each path. The following heat capacities for air may be assumed independent of temperature:

$$C_V = 20.78 \qquad \text{and} \qquad C_P = 29.10 \text{ J mol}^{-1} \text{ K}^{-1}$$

Assume also for air that PV/T is a constant, regardless of the changes it undergoes. At 298.15 K and 1 bar the molar volume of air is 0.02479 m^3 mol^{-1}.

Solution 2.9

In each case take the system as 1 mol of air contained in an imaginary piston/cylinder arrangement. Because the processes considered are mechanically reversible, the piston is imagined to move in the cylinder without friction. The final volume is:

$$V_2 = V_1 \frac{P_1}{P_2} = 0.02479 \left(\frac{1}{5}\right) = 0.004958\ \text{m}^3$$

(*a*) During the first step the air is cooled at the constant pressure of 1 bar until the final volume of 0.004958 m^3 is reached. The temperature of the air at the end of this cooling step is:

$$T' = T_1 \frac{V_2}{V_1} = 298.15 \left(\frac{0.004958}{0.02479}\right) = 59.63\ \text{K}$$

Whence,

$$\begin{aligned} Q &= \Delta H = C_P\, \Delta T = (29.10)(59.63 - 298.15) = -6{,}941\ \text{J} \\ \Delta U &= \Delta H - \Delta(PV) = \Delta H - P\, \Delta V \\ &= -6{,}941 - (1 \times 10^5)(0.004958 - 0.02479) = -4{,}958\ \text{J} \end{aligned}$$

During the second step the volume is held constant at V_2 while the air is heated to its final state. By Eq. (2.19),

$$\Delta U = Q = C_V\, \Delta T = (20.78)(298.15 - 59.63) = 4{,}958\ \text{J}$$

The complete process represents the sum of its steps. Hence,

$$Q = -6{,}941 + 4{,}958 = -1{,}983\ \text{J}$$

and

$$\Delta U = -4{,}958 + 4{,}958 = 0$$

Because the first law applies to the entire process, $\Delta U = Q + W$, and therefore,

$$0 = -1{,}983 + W \qquad \text{whence} \qquad W = 1{,}983\ \text{J}$$

Equation (2.15), $\Delta H = \Delta U + \Delta(PV)$, also applies to the entire process. But $T_1 = T_2$, and therefore, $P_1V_1 = P_2V_2$. Hence $\Delta(PV) = 0$, and

$$\Delta H = \Delta U = 0$$

(*b*) Two different steps are used in this case to reach the same final state of the air. In the first step the air is heated at a constant volume equal to its initial value until the final pressure of 5 bar is reached. The air temperature at the end of this step is:

$$T' = T_1 \frac{P_2}{P_1} = 298.15 \left(\frac{5}{1}\right) = 1{,}490.75\ \text{K}$$

For this step the volume is constant, and

$$Q = \Delta U = C_V \, \Delta T = (20.78)(1{,}490.75 - 298.15) = 24{,}788 \text{ J}$$

In the second step the air is cooled at $P = 5$ bar to its final state:

$$Q = \Delta H = C_P \, \Delta T = (29.10)(298.15 - 1{,}490.75) = -34{,}703 \text{ J}$$

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - P \, \Delta V$$

$$= -34{,}703 - (5 \times 10^5)(0.004958 - 0.02479) = -24{,}788 \text{ J}$$

For the two steps combined,

$$Q = 24{,}788 - 34{,}703 = -9{,}915 \text{ J}$$

$$\Delta U = 24{,}788 - 24{,}788 = 0$$

$$W = \Delta U - Q = 0 - (-9{,}915) = 9{,}915 \text{ J}$$

and as before $\qquad \Delta H = \Delta U = 0$

The property changes ΔU and ΔH calculated for the given change in state are the same for both paths. On the other hand the answers to parts (*a*) and (*b*) show that Q and W depend on the path.

Example 2.10

Calculate the internal-energy and enthalpy changes that occur when air is changed from an initial state of 40(°F) and 10(atm), where its molar volume is 36.49(ft)^3(lb mole)$^{-1}$, to a final state of 140(°F) and 1(atm). Assume for air that PV/T is constant and that C_V= 5 and C_P= 7(Btu)(lb mole)$^{-1}$(°F)$^{-1}$.

Solution 2.10

Because property changes are independent of the process that brings them about, calculations may be based on a two-step, mechanically reversible process in which 1(lb mole) of air is (*a*) cooled at constant volume to the final pressure, and (*b*) heated at constant pressure to the final temperature. The absolute temperatures here are on the Rankine scale:

$$T_1 = 40 + 459.67 = 499.67(\text{R}) \qquad T_2 = 140 + 459.67 = 599.67(\text{R})$$

Because $PV = kT$, the ratio T/P is constant for step (*a*). The intermediate temperature between the two steps is therefore:

$$T' = (499.67)(1/10) = 49.97(\text{R})$$

and the temperature changes for the two steps are:

$$\Delta T_a = 49.97 - 499.67 = -449.70(\text{R})$$
$$\Delta T_b = 599.67 - 49.97 = 549.70(\text{R})$$

For step (*a*), by Eqs. (2.18) and (2.15),

$$\begin{aligned}\Delta U_a &= C_V\,\Delta T_a = (5)(-449.70) = -2{,}248.5(\text{Btu})\\ \Delta H_a &= \Delta U_a + V\,\Delta P_a\\ &= -2{,}248.5 + (36.49)(1-10)(2.7195) = -3{,}141.6(\text{Btu})\end{aligned}$$

The factor 2.7195 converts the PV product from $(\text{atm})(\text{ft})^3$, which is an energy unit, into (Btu).

For step (*b*), the final volume of the air is:

$$V_2 = V_1\frac{P_1T_2}{P_2T_1} = 36.49\left(\frac{10}{1}\right)\left(\frac{599.67}{499.67}\right) = 437.93(\text{ft})^3$$

By Eqs. (2.22) and (2.15),

$$\begin{aligned}\Delta H_b &= C_P\,\Delta T_b = (7)(549.70) = 3{,}847.9(\text{Btu})\\ \Delta U_b &= \Delta H_b - P\,\Delta V_b\\ &= 3{,}847.9 - (1)(437.93-36.49)(2.7195) = 2{,}756.2(\text{Btu})\end{aligned}$$

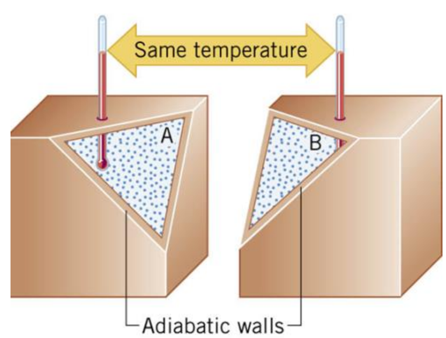
For the two steps together,

$$\begin{aligned}\Delta U &= -2{,}248.5 + 2{,}756.2 = 507.7(\text{Btu})\\ \Delta H &= -3{,}141.6 + 3{,}847.9 = 706.3(\text{Btu})\end{aligned}$$

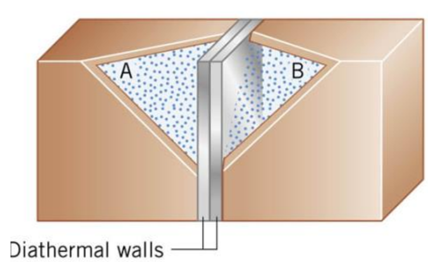
Zeroth Law of Thermodynamics:

- The forgotten Law of Science
- Two systems are said to be in thermal equilibrium if there is no heat flow between them when they are brought into contact.
- Temperature is the indicator of thermal equilibrium in the sense that there is no net flow of heat between two systems in thermal contact that have the same temperature.

Two systems individually in thermal equilibrium with a third system are in thermal equilibrium with each other.



(*a*)



(*b*)