

We begin by defining the first law of thermodynamics

$$\frac{dU}{dt} = Q + W \quad (1)$$

If we define the rate of work in a closed system and rearrange eqn 1 for Q

$$Q = \frac{dU}{dt} + P \frac{dV}{dt} \quad (2)$$

$$W = -P \frac{dV}{dt}$$

Now redefine the internal energy change as...

$$\frac{dU}{dt} = \frac{\delta U}{\delta T} \frac{dT}{dt} + \frac{\delta U}{\delta V} \frac{dV}{dt} \quad (3)$$

Now sub in eqn 3 into 2 and rearrange

$$Q = \frac{\delta U}{\delta T} \frac{dT}{dt} + \frac{\delta U}{\delta V} \frac{dV}{dt} + P \frac{dV}{dt}$$

$$= C_v \frac{dT}{dt} + \left(\frac{\delta U}{\delta V} + P \right) \frac{dV}{dt} \quad (4)$$

$$C_v = \frac{\delta U}{\delta T} \quad (5)$$

Under a constant volume process, we the change of internal energy with respect to temperature as the heat capacity under constant volume. Now introduce the definition of enthalpy and derive with respect to time. Then, rearrange for the change in internal energy and sub in eqn 2. Lastly, rearrange for Q

$$H = U + PV$$

$$\frac{dH}{dt} = \frac{dU}{dt} + P \frac{dV}{dt} + V \frac{dP}{dt}$$

$$\frac{dH}{dt} = Q - P \frac{dV}{dt} + P \frac{dV}{dt} + V \frac{dP}{dt}$$

$$Q = \frac{dH}{dt} - V \frac{dP}{dt} \quad (6)$$

Now similarly we can expand enthalpy...

$$\frac{dH}{dt} = \frac{\delta H}{\delta T} \frac{dT}{dt} + \frac{\delta H}{\delta P} \frac{dP}{dt} \quad (7)$$

Sub eqn 7 into 6

$$Q = \frac{\delta H}{\delta T} \frac{dT}{dt} + \frac{\delta U}{\delta P} \frac{dP}{dt} - V \frac{dP}{dt}$$

$$= \frac{\delta H}{\delta T} \frac{dT}{dt} + \left(\frac{\delta U}{\delta P} - V \right) \frac{dP}{dt}$$

$$= C_p \frac{dT}{dt} + \left(\frac{\delta U}{\delta P} - V \right) \frac{dP}{dt} \quad (8)$$

$$C_p = \frac{\delta H}{\delta T} \quad (9)$$

Under a constant pressure process, we express the change of enthalpy with respect to temperature as the heat capacity under constant pressure.

$$\begin{aligned}
 H &= U + PV \\
 \frac{dH}{dt} &= \frac{dU}{dt} + P \frac{dV}{dt} + V \frac{dP}{dt} \\
 \frac{\delta H}{\delta T} \frac{dT}{dt} + \frac{\delta H}{\delta P} \frac{dP}{dt} &= \frac{\delta U}{\delta T} \frac{dT}{dt} + \frac{\delta U}{\delta V} \frac{dV}{dt} + P \frac{dV}{dt} + V \frac{dP}{dt}
 \end{aligned} \tag{10}$$

If we expand the volume time derivatives...

$$\frac{dV}{dt} = \frac{\delta V}{\delta T} \frac{dT}{dt} + \frac{\delta V}{\delta P} \frac{dP}{dt}$$

Sub these into eqn 10 and rearrange.

$$\begin{aligned}
 \frac{\delta H}{\delta T} \frac{dT}{dt} + \frac{\delta H}{\delta P} \frac{dP}{dt} &= \frac{\delta U}{\delta T} \frac{dT}{dt} + \frac{\delta U}{\delta V} \left(\frac{\delta V}{\delta T} \frac{dT}{dt} + \frac{\delta V}{\delta P} \frac{dP}{dt} \right) + P \left(\frac{\delta V}{\delta T} \frac{dT}{dt} + \frac{\delta V}{\delta P} \frac{dP}{dt} \right) + V \frac{dP}{dt} \\
 \frac{\delta H}{\delta T} \frac{dT}{dt} - \frac{\delta U}{\delta T} \frac{dT}{dt} - \frac{\delta U}{\delta V} \frac{\delta V}{\delta T} \frac{dT}{dt} - P \frac{\delta V}{\delta T} \frac{dT}{dt} + \frac{\delta H}{\delta P} \frac{dP}{dt} - V \frac{dP}{dt} - \frac{\delta U}{\delta V} \frac{\delta V}{\delta P} \frac{dP}{dt} - P \frac{\delta V}{\delta P} \frac{dP}{dt} &= 0 \\
 \left(\frac{\delta H}{\delta T} - \frac{\delta U}{\delta T} - \frac{\delta U}{\delta V} \frac{\delta V}{\delta T} - P \frac{\delta V}{\delta T} \right) \frac{dT}{dt} + \left(\frac{\delta H}{\delta P} - V - \frac{\delta U}{\delta V} \frac{\delta V}{\delta P} - P \frac{\delta V}{\delta P} \right) \frac{dP}{dt} &= 0
 \end{aligned} \tag{11}$$

To use this relation in eqn 11, both $\frac{dP}{dt}$ and $\frac{dT}{dt}$ must be zero. For $\frac{dT}{dt}$, this relation becomes...

$$\begin{aligned}
 \left(\frac{\delta H}{\delta T} - \frac{\delta U}{\delta T} - \frac{\delta U}{\delta V} \frac{\delta V}{\delta T} - P \frac{\delta V}{\delta T} \right) \frac{dT}{dt} &= 0 \\
 \frac{\delta H}{\delta T} - \frac{\delta U}{\delta T} - \frac{\delta U}{\delta V} \frac{\delta V}{\delta T} - P \frac{\delta V}{\delta T} &= 0 \\
 \frac{\delta H}{\delta T} &= \frac{\delta U}{\delta T} + \frac{\delta U}{\delta V} \frac{\delta V}{\delta T} + P \frac{\delta V}{\delta T}
 \end{aligned} \tag{12}$$

Using the definitions of the heat capacity under constant pressure and heat capacity under constant volume in eqn 13

$$\begin{aligned}
 \left(\frac{\delta H}{\delta T} - \frac{\delta U}{\delta T} - \frac{\delta U}{\delta V} \frac{\delta V}{\delta T} - P \frac{\delta V}{\delta T} \right) \frac{dT}{dt} &= 0 \\
 \frac{\delta H}{\delta T} - \frac{\delta U}{\delta T} - \frac{\delta U}{\delta V} \frac{\delta V}{\delta T} - P \frac{\delta V}{\delta T} &= 0 \\
 C_p &= C_v + \frac{\delta U}{\delta V} \frac{\delta V}{\delta T} + P \frac{\delta V}{\delta T}
 \end{aligned} \tag{13}$$

Utilizing Joule's law, we know that the internal energy does not change as volume changes in an ideal gas (i.e., $\frac{\delta U}{\delta V} = 0$)

$$C_p = C_v + P \frac{\delta V}{\delta T} \tag{14}$$

Recall this volume derivative is under constant pressure...therefore using the ideal gas law.

$$\begin{aligned}
 PV &= nKT \\
 P \frac{\delta V}{\delta T} &= nK
 \end{aligned} \tag{15}$$

Sub eqn 16 into 14

$$C_p = C_v + nK \tag{16}$$

Divide by unit mass or unit mole to yield the relations with specific heat capacity

$$\begin{aligned} c_p &= c_v + R \\ c_{p,m} &= c_{v,m} + \mathfrak{R} \end{aligned}$$