

Chapter 4

Applications of the First Law

Min Soo Kim

Seoul National University

4.1 Heat Capacity

The heat capacity C

$$C = \lim_{\Delta T \rightarrow 0} \left(\frac{Q}{\Delta T} \right) = \frac{\delta Q}{dT} \quad Q = m c \Delta T$$

Specific heat capacity = heat capacity per unit mass

$$c = \frac{1}{m} \left(\frac{\delta Q}{dT} \right) = \frac{\delta q}{dT}$$

4.1 Heat Capacity

The **specific heat** c_v , where the heat is supplied at constant volume

$$c_v = \left(\frac{\delta Q}{dT} \right)_v$$

The **specific heat** c_p , where the heat is supplied at constant pressure

$$c_p = \left(\frac{\delta Q}{dT} \right)_p$$

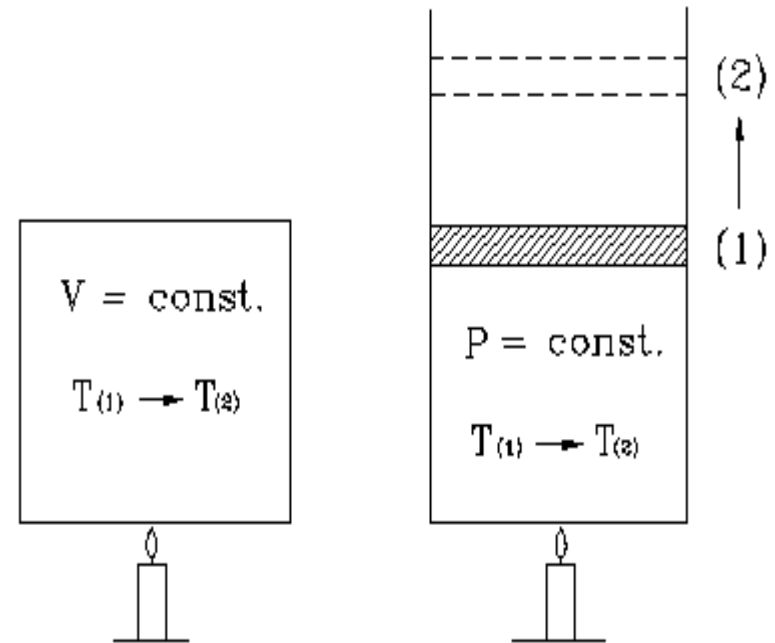


Figure 4.1 Heat addition on different conditions [2]

[2] <http://cfile25.uf.tistory.com/image/246FE841534790190378A0>

4.1 Heat Capacity

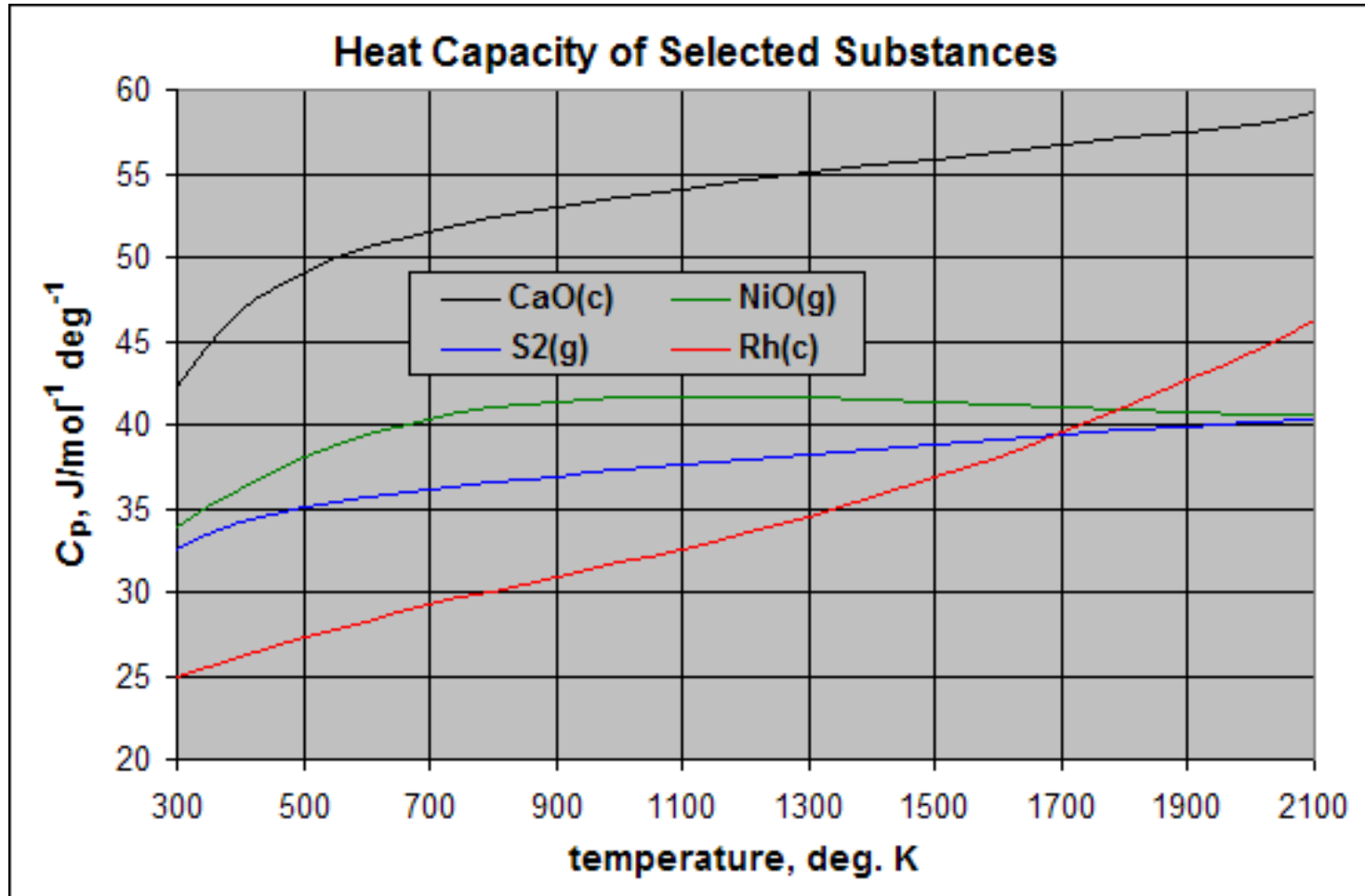


Figure 4.2 Heat capacity of selected substances [3]

[3] https://upload.wikimedia.org/wikipedia/en/c/cb/Heat_Capacity_of_Selected_Substances.PNG

4.1 Heat Capacity

Water Specific Heat Capacity vs Temperature ($p = 1 \text{ bar}$)

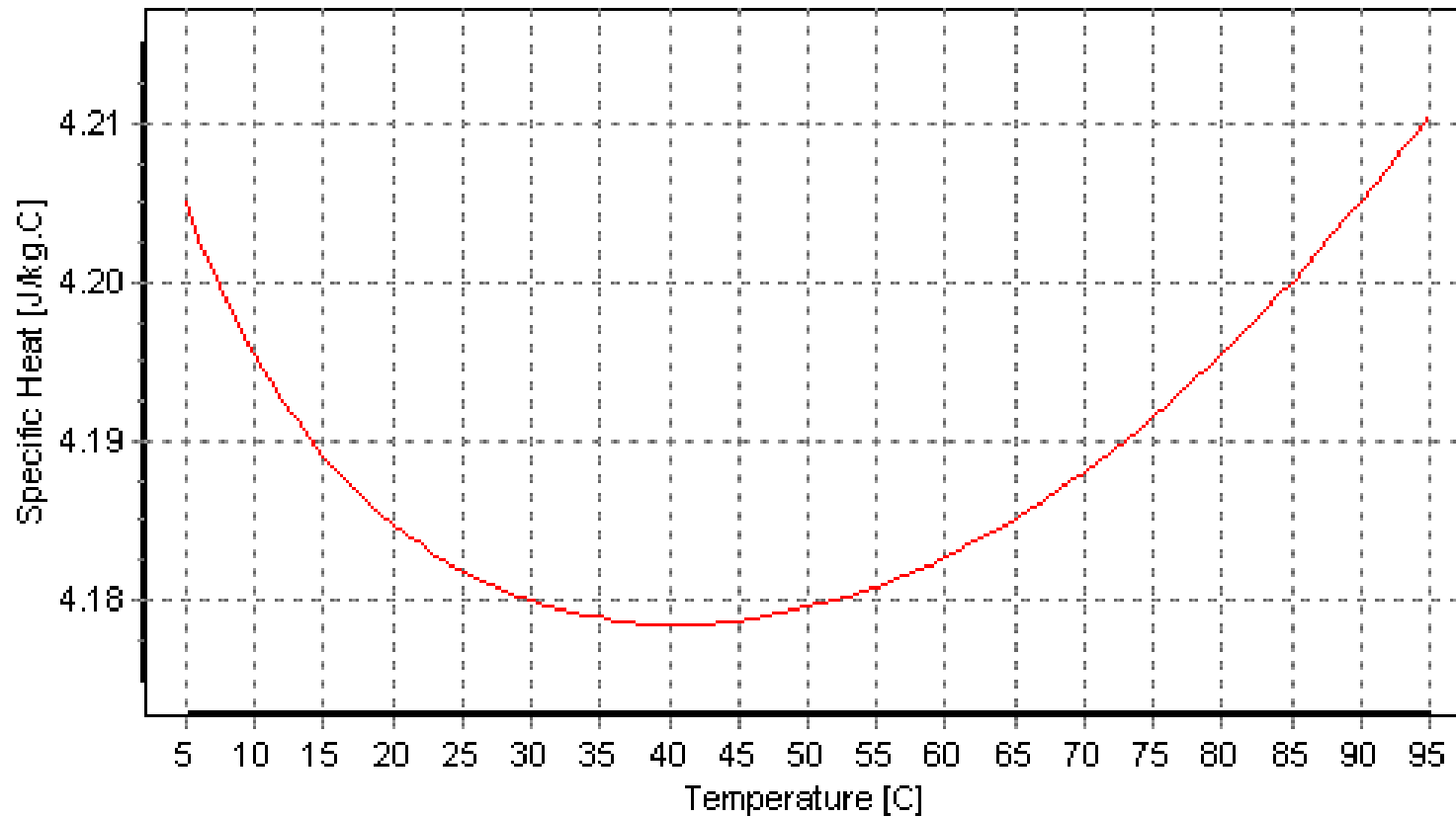


Figure 4.3 Water Heat capacity [4]

[4] <http://physics.stackexchange.com/questions/287910/why-water-heat-capacity-has-minimum-at-body-temperature>

4.2 Mayer's Equation

We wish to find the relationship between c_v and c_p for an ideal gas

$$dU = \delta Q - PdV$$

$$du = \delta q - Pdv$$

$$u = u(v, T) \xrightarrow{\text{Ideal gas}} u = u(T)$$

the equation of state is $Pv = RT$

$$du = \left(\frac{\partial u}{\partial v} \right)_T dv + \left(\frac{\partial u}{\partial T} \right)_v dT$$

4.2 Mayer's Equation

$$\delta q = \left(\frac{\partial u}{\partial T} \right)_v dT + \left[\left(\frac{\partial u}{\partial v} \right)_T + P \right] dv$$

To obtain c_v , we divide this equation by dT and hold the volume constant so that $dv=0$. The result, which holds for any reversible process is

$$c_v = \left(\frac{\delta q}{dT} \right)_v = \left(\frac{\partial u}{\partial T} \right)_v$$

This follows from the Gay-Lussac-Joule experiment. Thus

$$\left(\frac{\partial u}{\partial v} \right)_T = 0$$

4.2 Mayer's Equation

$$\delta q = c_v dT + P dv$$

$$P dv + v dP = R dT$$

$$\delta q = (c_v + R) dT - \cancel{v dP} \quad \text{For constant pressure}$$

$$c_p = \left(\frac{\delta q}{dT} \right)_p \Rightarrow \left(\frac{\delta q}{dT} \right)_p = c_v + R = c_p$$

$$\therefore c_p = c_v + R \quad \text{Mayer's equation}$$

$$\gamma = \frac{c_p}{c_v} \quad \text{The ratio of specific heat capacities}$$

4.3 Enthalpy and Heats of Transformation

Types of heat transfer

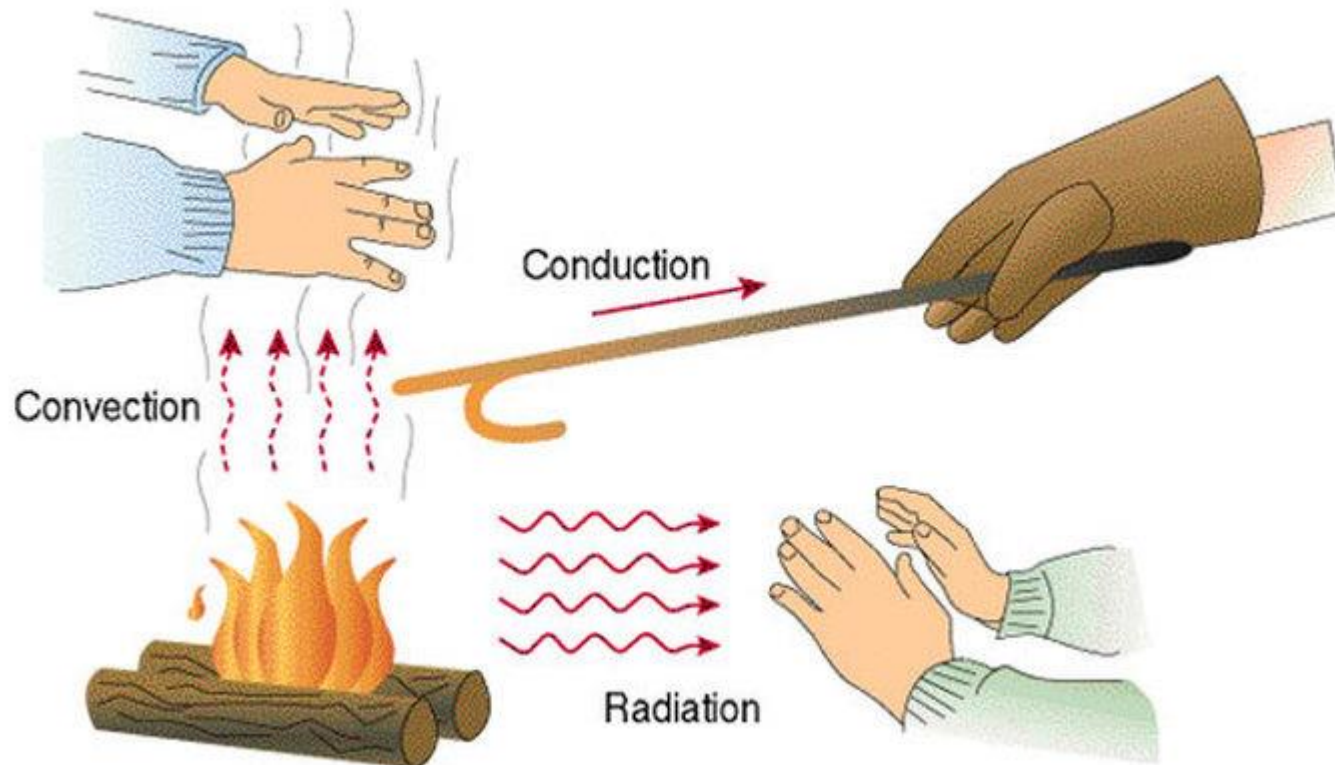


Figure 4.4 Types of heat transfer [5]

[5] <http://www.spectrose.com/wp-content/uploads/2012/12/modes-of-heat-transfer-conduction-convection-and-radiation.jpg>

4.3 Enthalpy and Heats of Transformation

The heat of transformation is the heat transfer accompanying a phase change. A change of phase is an isothermal and isobaric process and entails a change of volume, so work is always done on or by a system in a phase change.

$$w = P(v_2 - v_1)$$

$$du = \delta q - Pdv$$

Or, for a finite change, $(u_2 - u_1) = l - P(v_2 - v_1)$

$$l = (u_2 + Pv_2) - (u_1 + Pv_1)$$

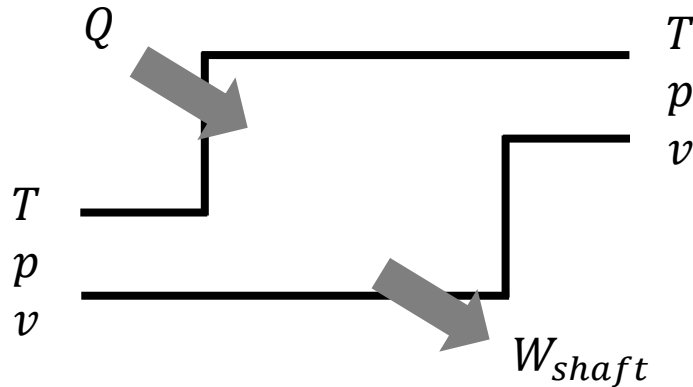
l is the **latent heat** of transformation per kilomole associated with a given phase change (for constant T and P)

4.3 Enthalpy and Heats of Transformation

Let $h \equiv u + Pv$ h is the specific enthalpy.

Since u , p , and v are all state variables, h is also a state variable.

$$\text{So, } l = \int dq = (u_2 - u_1) + p(v_2 - v_1) = h_2 - h_1$$



\therefore the latent heat of transformation is equal to the difference in enthalpies of the two phases.

4.4 Relationships Involving Enthalpy

$$h = h(T, P) \quad dh = \left(\frac{\partial h}{\partial T} \right)_P dT + \left(\frac{\partial h}{\partial P} \right)_T dP$$

$$h = u + Pv \quad dh = du + Pdv + vdP$$

$$\delta q = du + Pdv = dh - vdP$$

$$\delta q = \left(\frac{\partial h}{\partial T} \right)_P dT + \left[\left(\frac{\partial h}{\partial P} \right)_T - v \right] dP$$

4.4 Relationships Involving Enthalpy

Since $c_p = \left(\frac{\delta q}{dT}\right)_p$

From previous equation, we can get $c_p = \left(\frac{\partial h}{\partial T}\right)_p$

From the result of the Joule-Thomson experiment, it will be shown that

$$\left(\frac{\partial h}{\partial P}\right)_T = 0$$

For an ideal gas. Then $\delta q = c_p dT - v dP$

Thus, for an ideal gas $c_p = \left(\frac{\partial h}{\partial T}\right)_p = \frac{dh}{dT}$

4.5 Comparison of u and h

The parallel expressions involving the internal energy and the enthalpy

Table Analogous relations involving the internal energy and the enthalpy

	Internal energy u	Enthalpy h
Reversible process	$du = \delta q - Pdv$	$dh = \delta q + vdP$
	$c_v = \left(\frac{\partial u}{\partial T}\right)_v$	$c_p = \left(\frac{\partial h}{\partial T}\right)_p$
Ideal gas	$\delta q = c_v dT + Pdv$	$\delta q = c_p dT - vdP$
	$\left(\frac{\partial u}{\partial v}\right)_T = 0$	$\left(\frac{\partial h}{\partial P}\right)_T = 0$

4.5 Comparison of u and h

Thermodynamic potentials: relations of the internal energy and the enthalpy

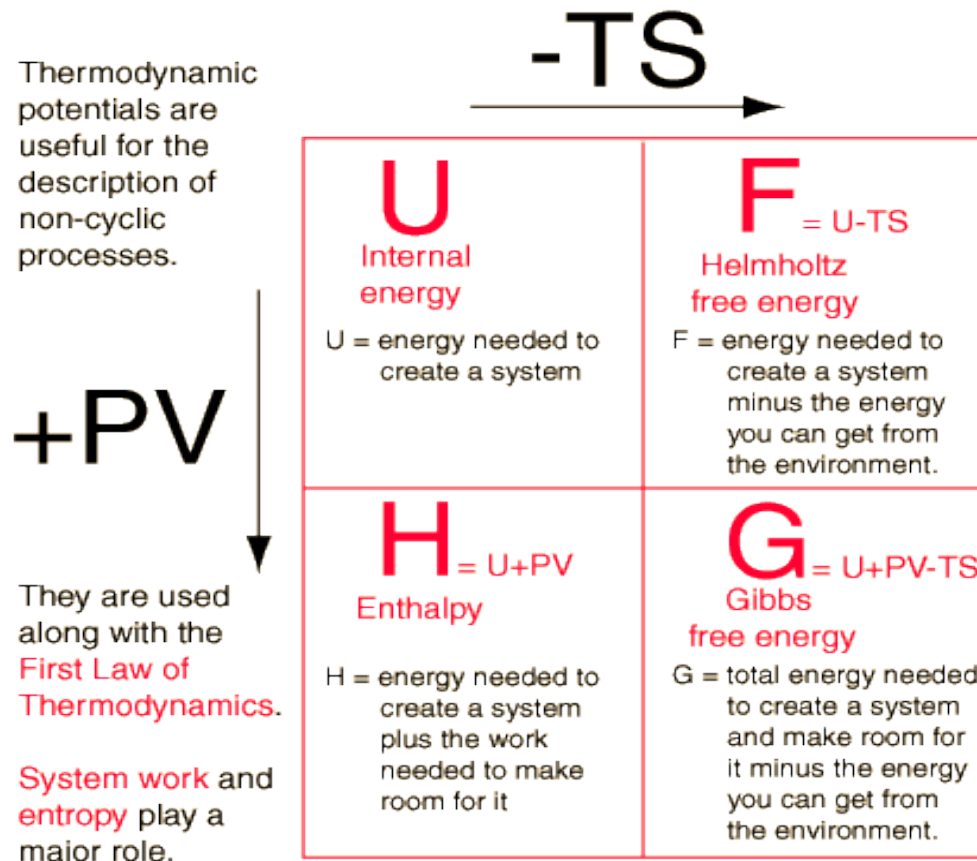


Figure 4.5 Relations of Thermodynamic potentials [8]

[8] <http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/imgheat/tpot2.gif>

4.6 Work Done in an Adiabatic Process

We now wish to find the specific work done in an adiabatic process involving An ideal gas. Setting $\delta q = 0$ in $\delta q = c_p dT - v dP$, we obtain

$$v dP = c_p dT$$

We also have

$$\delta q = c_v dT + P dv$$

Which for $\delta q = 0$ yields

$$P dv = -c_v dT$$

$$\frac{v dP}{p dv} = -\frac{c_p}{c_v} = -\gamma \quad \text{or} \quad \frac{dP}{P} = -\gamma \frac{dv}{v}$$

4.6 Work Done in an Adiabatic Process

This equation can be easily integrated to give

$$Pv^\gamma = K$$

Where K is constant of integration. This is the relationship between the pressure and volume for an adiabatic process involving an ideal gas. Since $\gamma > 1$, it follows that P falls off more rapidly with v for an adiabatic process than it does for an isothermal process (for which $Pv = \text{constant}$)

The work done in the adiabatic process is

$$w = \int Pdv = K \int_{v_1}^{v_2} v^{-\gamma} dv = \frac{1}{1-\gamma} (Kv^{1-\gamma}) \Big|_{v_1}^{v_2}$$

4.6 Work Done in an Adiabatic Process

Now, $K = Pv^\gamma$ at both limits: if we use $K = P_2v_2^\gamma$ at the upper limit and $K = P_1v_1^\gamma$ at the lower limit, we obtain

$$w = \frac{1}{1 - \gamma} [P_2v_2 - P_1v_1]$$

For an expansion, $v_2 > v_1, w > 0$, and the work is done by the gas: for a compression the work is done by the surroundings on the gas. Note that for a reversible adiabatic process, $w = u_1 - u_2 = c_v(T_1 - T_2)$, which is another useful Expression for an ideal gas.