

Chapter 3

The First Law of Thermodynamics

Min Soo Kim

Seoul National University

3.1 Configuration work

Configuration work = Work in a reversible process $\delta W = \sum_i y_i dX_i, i=1, 2, \dots n.$

Change in the volume (ΔV) of the cylinder housing of a piston is $\Delta V = A\Delta h$ as the piston moves.

The work performed by the surroundings on the system as the piston moves inward is given by $W = P_{ext}\Delta V$

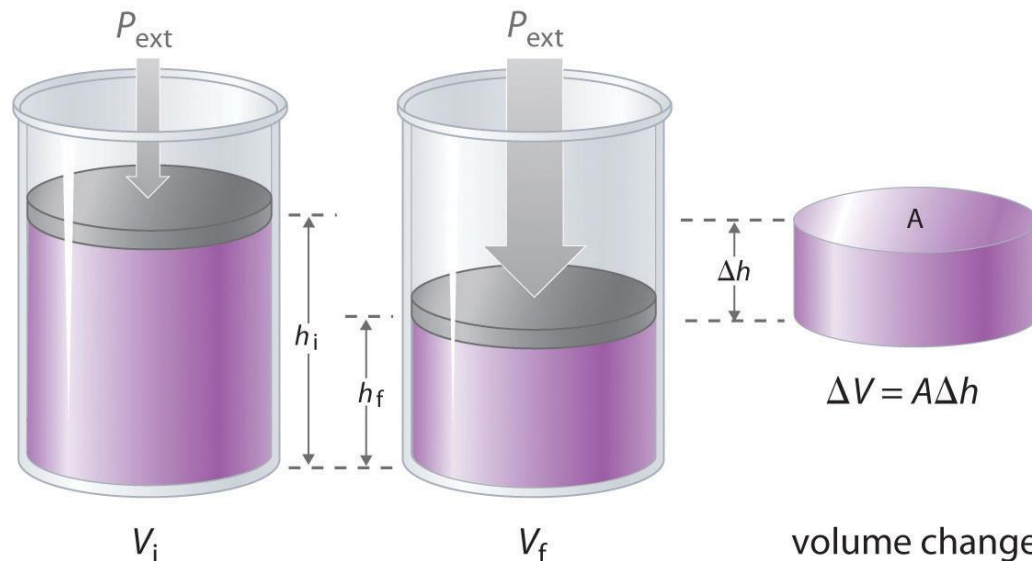


Figure 3.1 The work performed by the surroundings on the system [1]

[1] <http://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0/s22-01-thermodynamics-and-work.html>

3.1 Configuration work

Various examples of configuration work

System	Intensive Variable	Extensive Variable	δW
Gas, liquid or solid	P (pressure)	V (volume)	PdV
Film	Γ (surface tension)	A (area)	ΓdA
Electrolytic cell	ε (electromotive force)	q (charge)	εdq
Physical object	F (force)	s (distance)	Fds
Dielectric material	E (electric field)	P (polarization)	EdP

3.1 Configuration work

For isobaric process ($P=\text{constant}$)

$$W = \int_{V_A}^{V_B} \delta W = \int_{V_A}^{V_B} P dV = P(V_B - V_A)$$

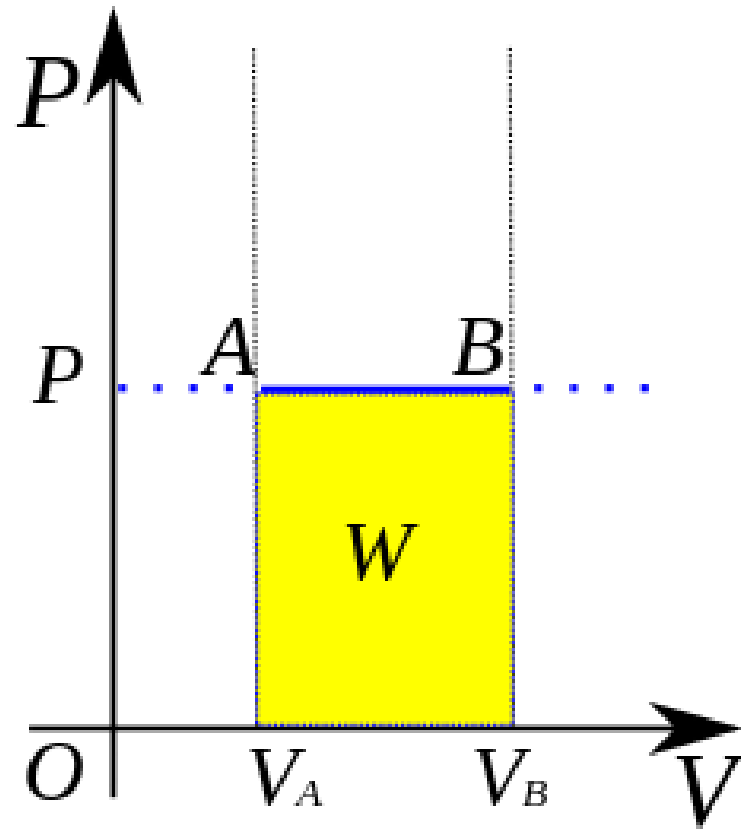


Figure 3.2 The yellow area represents the work done [2]

[2] https://en.wikipedia.org/wiki/Isobaric_process#/media/File:Isobaric_process_plain.svg

3.1 Configuration work

For isothermal process (ideal gas)

$$W = \int_{V_A}^{V_B} P dV = \int_{V_A}^{V_B} \frac{n\bar{R}T}{V} dV = n\bar{R}T \ln\left(\frac{V_B}{V_A}\right)$$

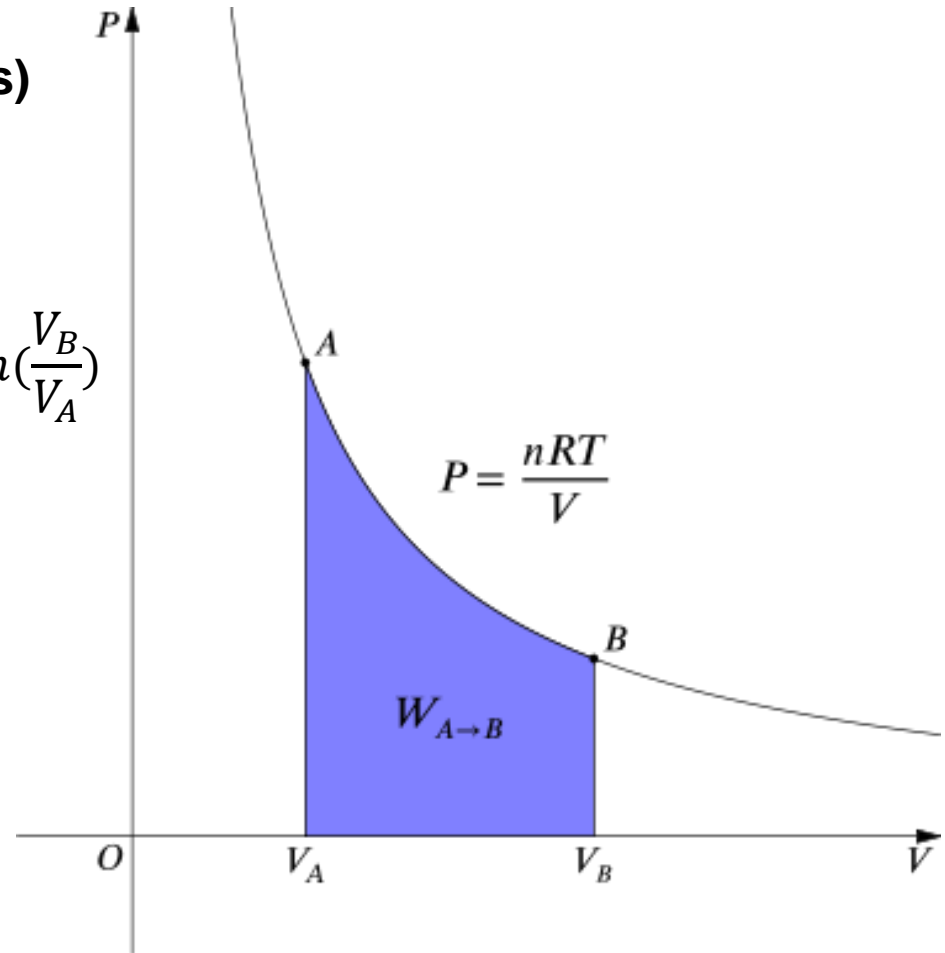
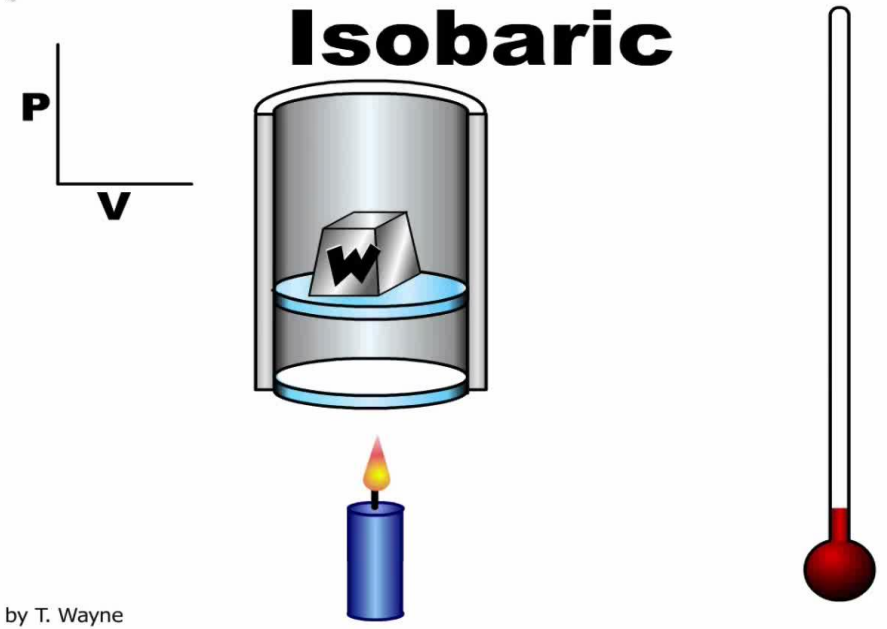
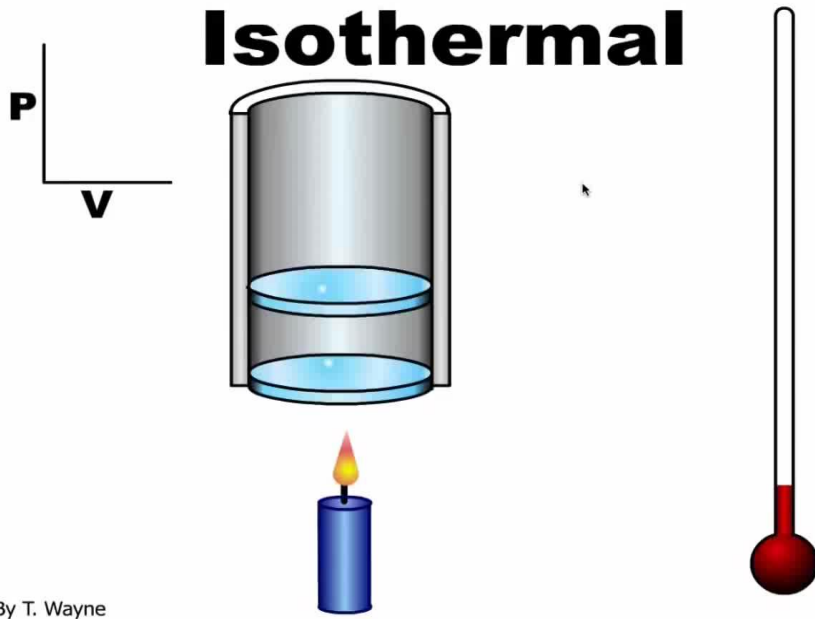


Figure 3.3 The purple area represents the work for this isothermal change [3]

[3] https://en.wikipedia.org/wiki/Isothermal_process#/media/File:Isothermal_process.svg

3.1 Configuration work

Video clips: isothermal and isobaric animation [4], [5]



[4] <https://www.youtube.com/watch?v=7doEaDtJtFs>
[5] <https://www.youtube.com/watch?v=CEBoFGkNaFQ>

3.1 Configuration work

Work is not a property of the system:

W is not a state variable. Since $\int PdV$ is the area under the curve, different results are obtained for paths 1 and 2.

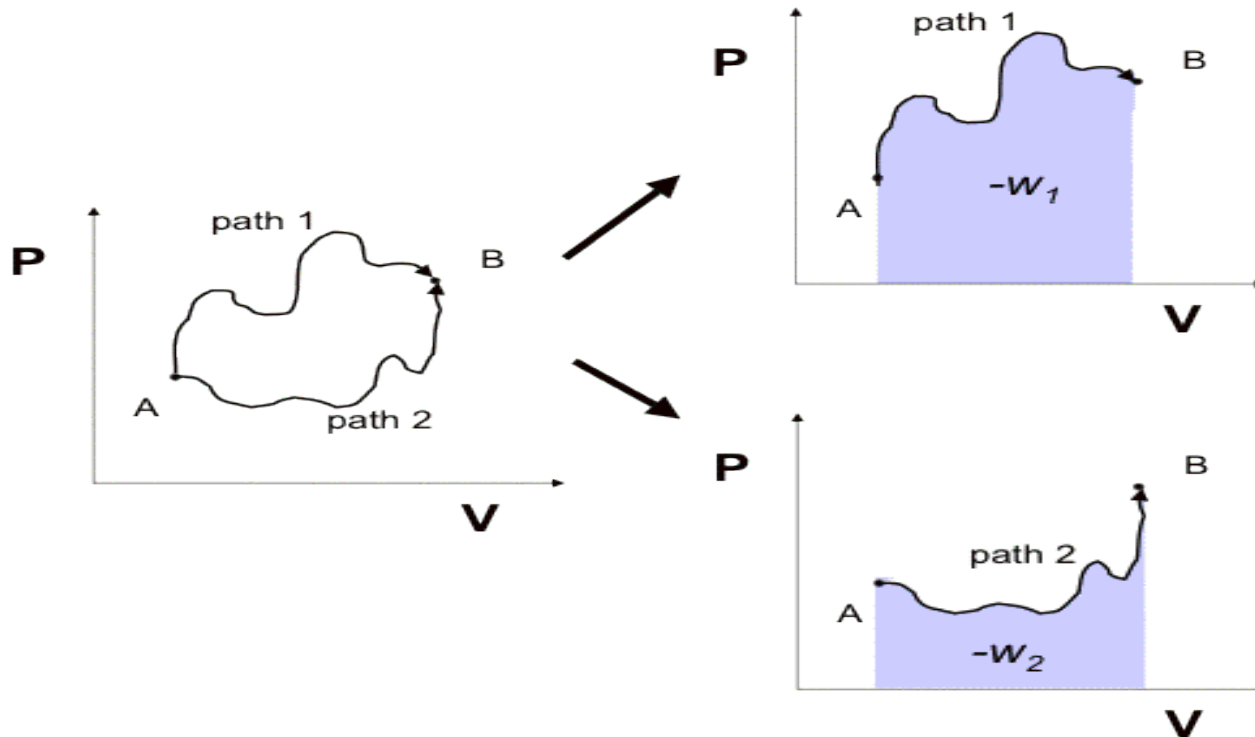


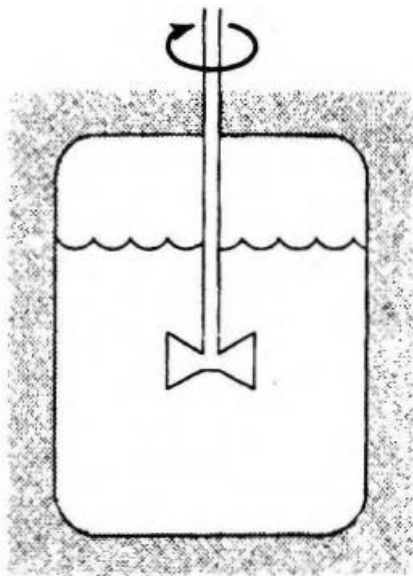
Figure 3.4 Work is path-dependent: the area under path 1 is different from the area under path 2 [6]

[6] <http://web.mit.edu/djirvine/www/3.012/3.012%20lectures/3.012%20lect03/3.012%20lect03.htm>

3.2 Dissipative work

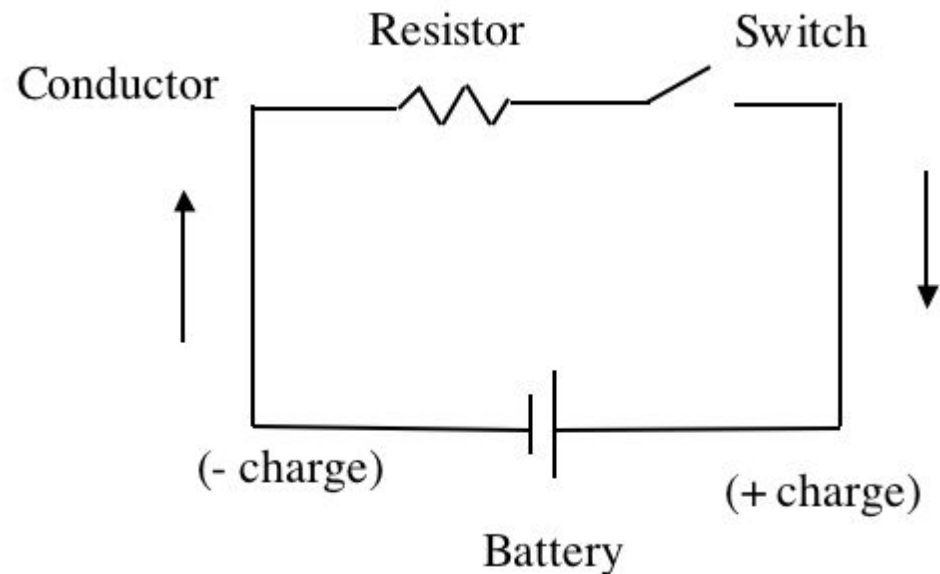
Dissipative work is work done in an irreversible process

A example of dissipative work is the work needed to maintain an electric current I in a resistor of resistance R



$$\delta W = -\tau d\theta$$

Figure 3.5 Stirring work. A stirrer is immersed in a fluid and an external torque is applied.



$$\delta W = -I^2 R dt$$

Figure 3.6 Electrical work. A current is passed through a resistor [7]

[7]http://educade.org/system/pictures/attachments/516f/3650/b381/5809/d300/0005/original/Basic_Electric_Board.png

3.3 Adiabatic work and internal energy

The total work done in all adiabatic processes between any two equilibrium states is **independent of the path**.

The work done on the system (with no heat flow) results in an increase in its **internal energy**

$$W_{ad} = \int_a^b \delta W_{ad}$$

$$dU = -\delta W_{ad}$$

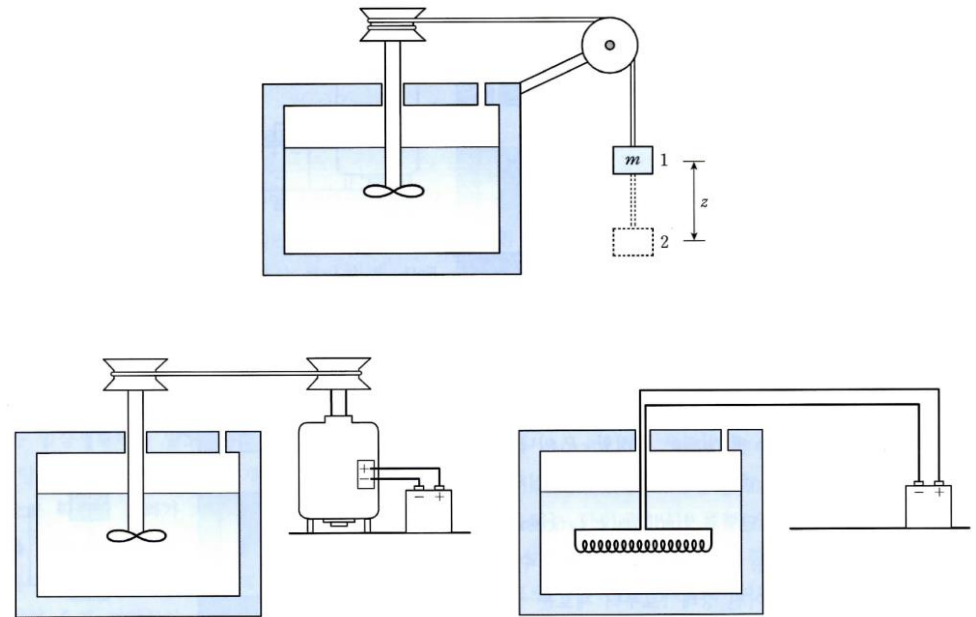


Figure 3.7 Three different adiabatic processes from state a to state b

3.4 Heat

Under adiabatic conditions, for which $dU = -\delta W_{ad}$. If the conditions are not so specialized in general. Instead we may write the equation

$$dU = \delta Q - \delta W$$

Heat flow into the system is equal to the total work done by the system minus the adiabatic work done

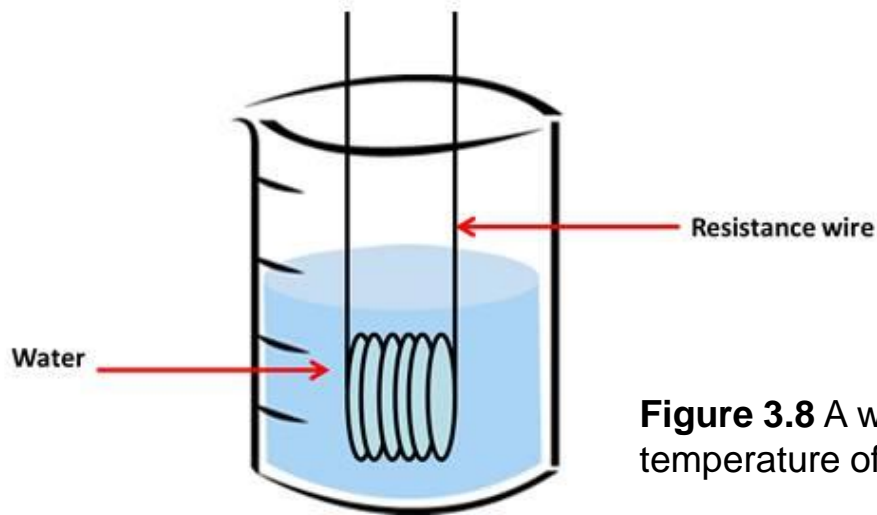


Figure 3.8 A way of raising the temperature of water by electrical work [8]

[8]http://physics.taskermilward.org.uk/KS4/core/heat_transfer/specific_heat_capacity/NichromeWireInWater.jpg

3.4 Heat

In words, the first law states that

The heat supplied is equal to the increase in internal energy of the system plus the work done by the system. Energy is conserved if heat is taken into account

Note that heat is not a property (state variable) of the system; only the internal energy is.

It can be shown that the quantity δQ exhibits the properties that are Commonly associated with heat.

These properties are summarized as follows.

1. The addition of heat to a body changes its state.
2. Heat may be conveyed from one body to another by conduction, convection, or radiation.
3. In a calorimetric experiment by the method of mixtures, heat is conserved, if the experimental bodies are adiabatically enclosed.

3.4 Heat

Modes of heat energy transfer: Conduction, Convection, Radiation

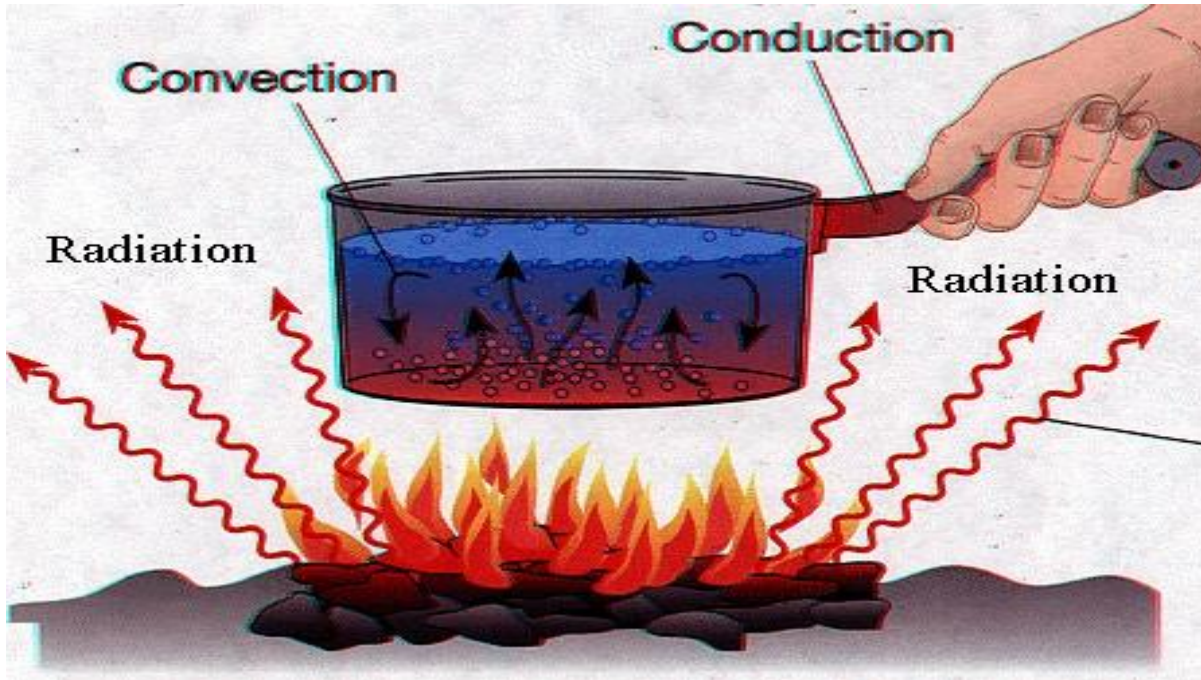


Figure 3.9 Modes of heat energy transfer [9]

[9] https://2.bp.blogspot.com/-VEB7KL43kEc/V3FURhV8aYI/AAAAAAAAABS0/lpR2nr6WP5423kiDgdY2_H7NkC6pKmS6gCLcB/s1600/heattransfer.jpg

3.7 Summary of the first law

1. Energy is conserved. Heat is energy transferred to a system causing a change in its internal energy minus any work done in the process.
2. The quantity U is a generalized store of energy possessed by a thermodynamic system which can be changed by adding or subtracting energy in any form.
3. The internal energy U is a state variable: it is extensive.

4. The first law can be expressed in differential form as

$$\delta Q = dU + \delta W$$

5. For a reversible process, δW is solely configuration (“PdV”) work, so that

$$\delta Q = dU + PdV$$

Chapter 4

Applications of the First Law

Min Soo Kim

Seoul National University

4.1 Heat Capacity

The heat capacity C

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

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

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

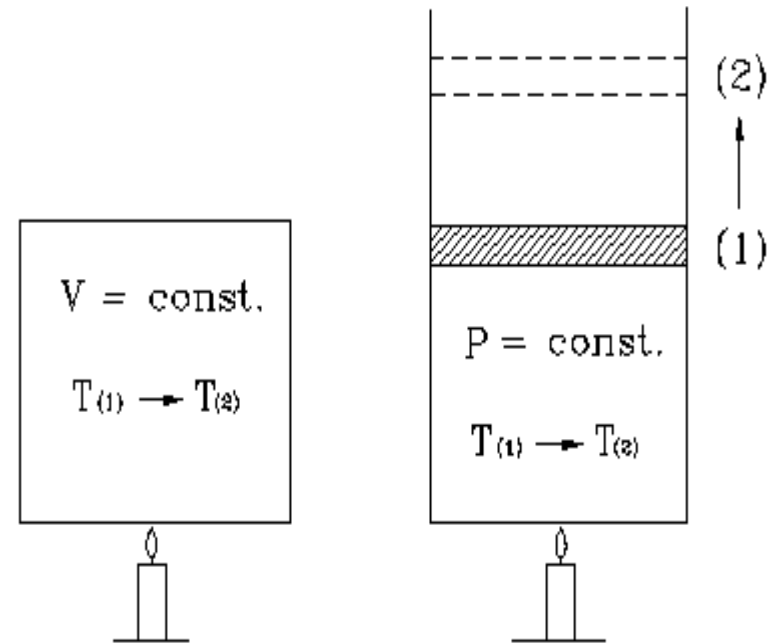


Figure 4.1 Heat addition on different conditions [2]

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

4.1 Heat Capacity

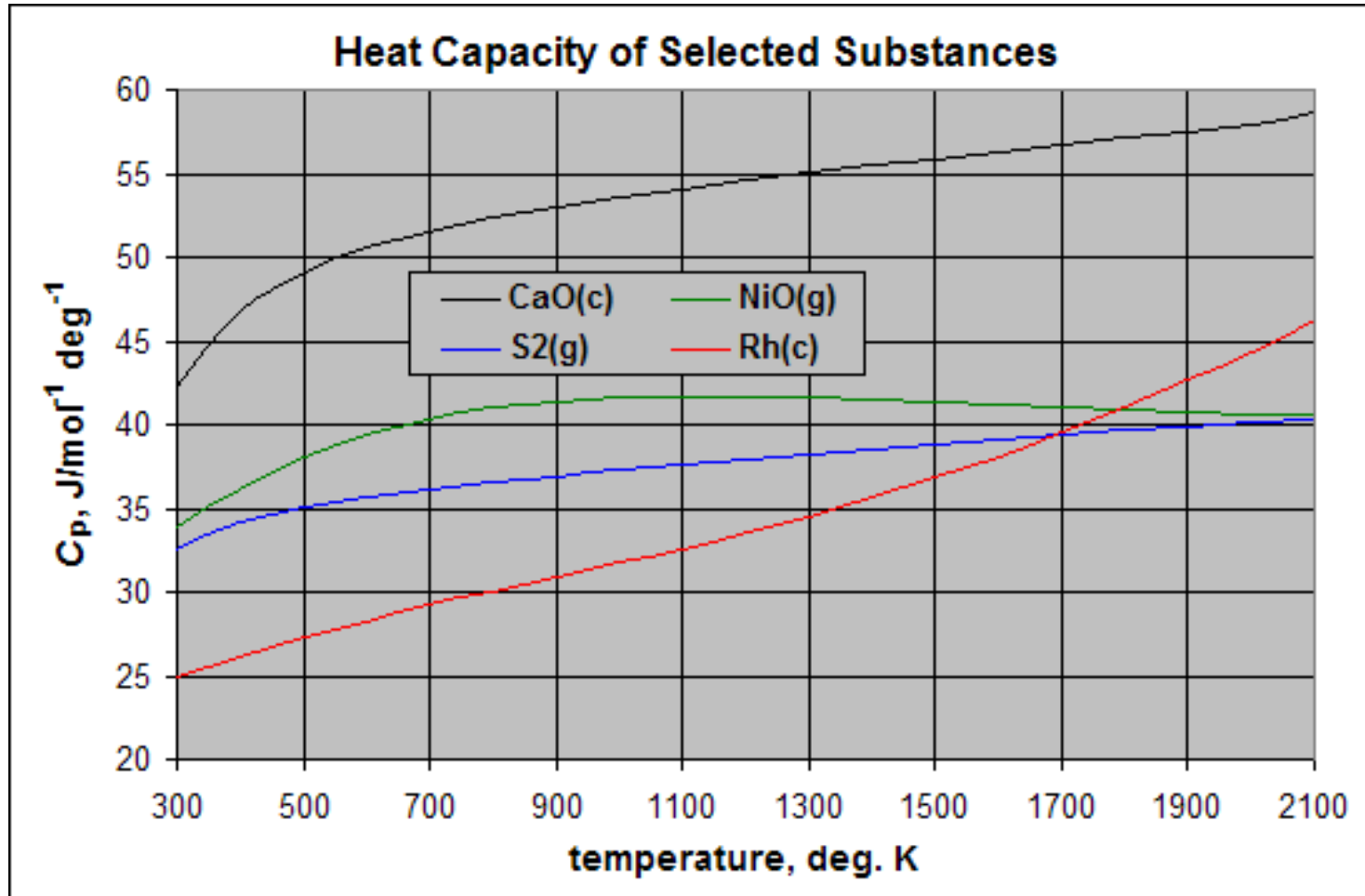


Figure 4.2 Heat capacity of selected substances [3]

[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 ($p = 1 \text{ bar}$)

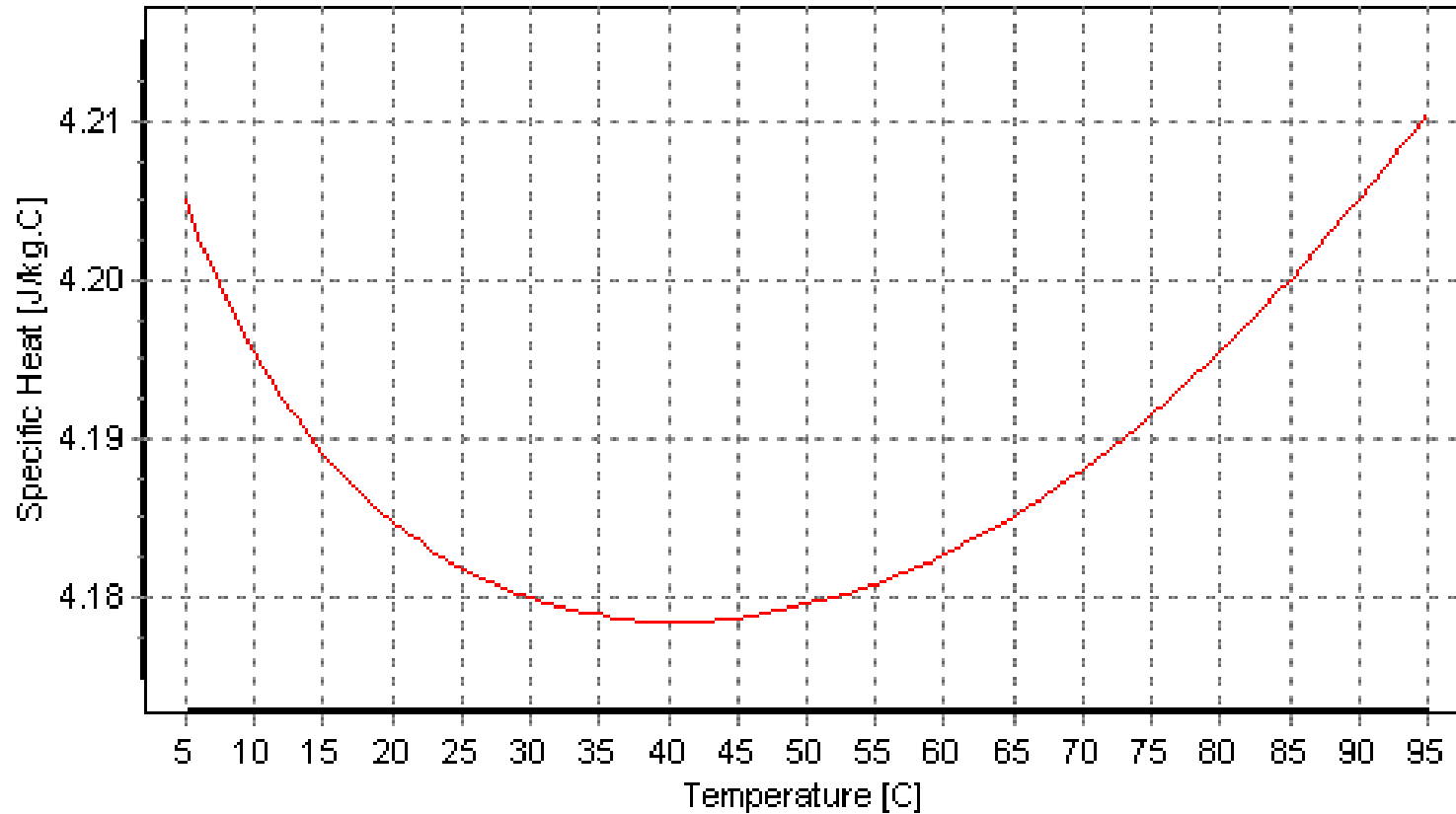


Figure 4.3 Water Heat capacity [4]

[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

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

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

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

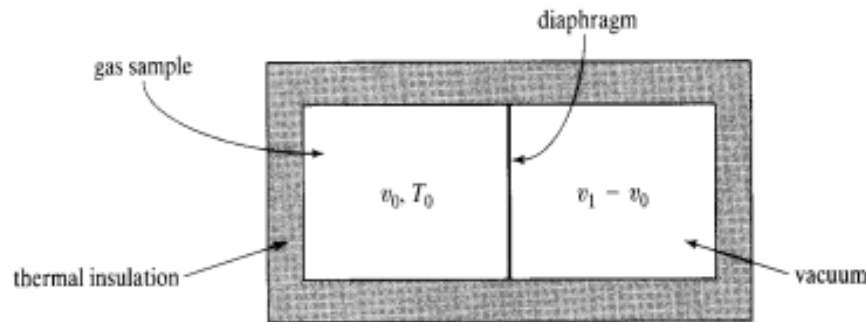
$$c_p = \left(\frac{\delta q}{dT} \right)_p \Rightarrow \left(\frac{\delta q}{dT} \right)_p = c_v + R = c_p$$

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

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

1. Gay-Lussac–Joule Experiment

In this experiment, an adiabatic chamber (thermally insulating walls which allow no heat transfer) with two compartments separated by a breakable diaphragm is constructed. We consider the state of the gas to be determined by (V, T) since P is fixed by the equation of state. Gas of volume V_1 , and temperature T_1 is introduced into one of the compartments while in the other there is a vacuum. When the diaphragm is broken, the gas undergoes a “free” expansion which does *NO* work. The gas has a new volume and potentially a new temperature which can be measured. However *NO* temperature change is observed!



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, $(u_2 - u_1) = l - P(v_2 - v_1)$

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

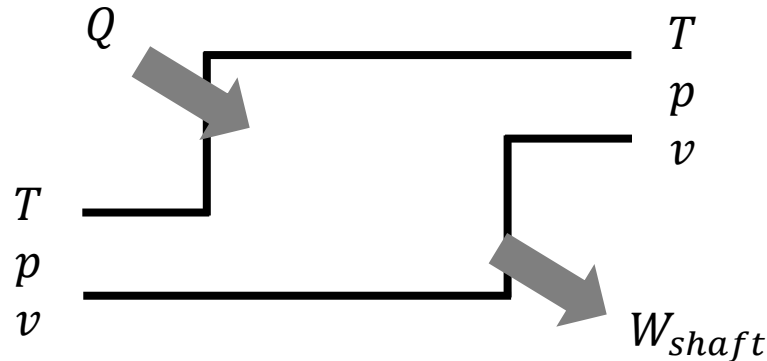
l is the **latent heat** of transformation per kilomole associated with a given phase change (for constant T and P)

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

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

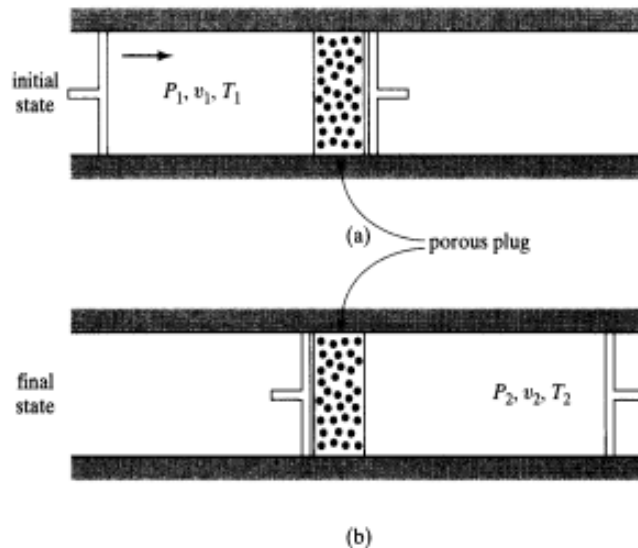
for an ideal gas.

Then $\delta q = c_p dT - v dP$

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

2. Joule-Thompson Experiment

In this experiment, an adiabatic cylinder is constructed with a porous plug in the middle. A gas in state (P_1, V_1, T_1) is introduced on one side of the porous plug and held in place by a piston which is able to move and which can push the gas through the porous plug. Another piston is placed on the other side of the porous plug. Initially it is placed right up against the porous plug so that the volume of gas on the other side of the cylinder is 0. When the piston is pressed into the adiabatic metal cylinder, gas will be forced through the porous plug, and collect on the other side. When all of the gas has been pushed through, the gas on the other side of the plug is in state (P_2, V_2, T_2) . Experimentally, it is found that while $T_1 = T_2$ while $P_1 \neq P_2$.



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

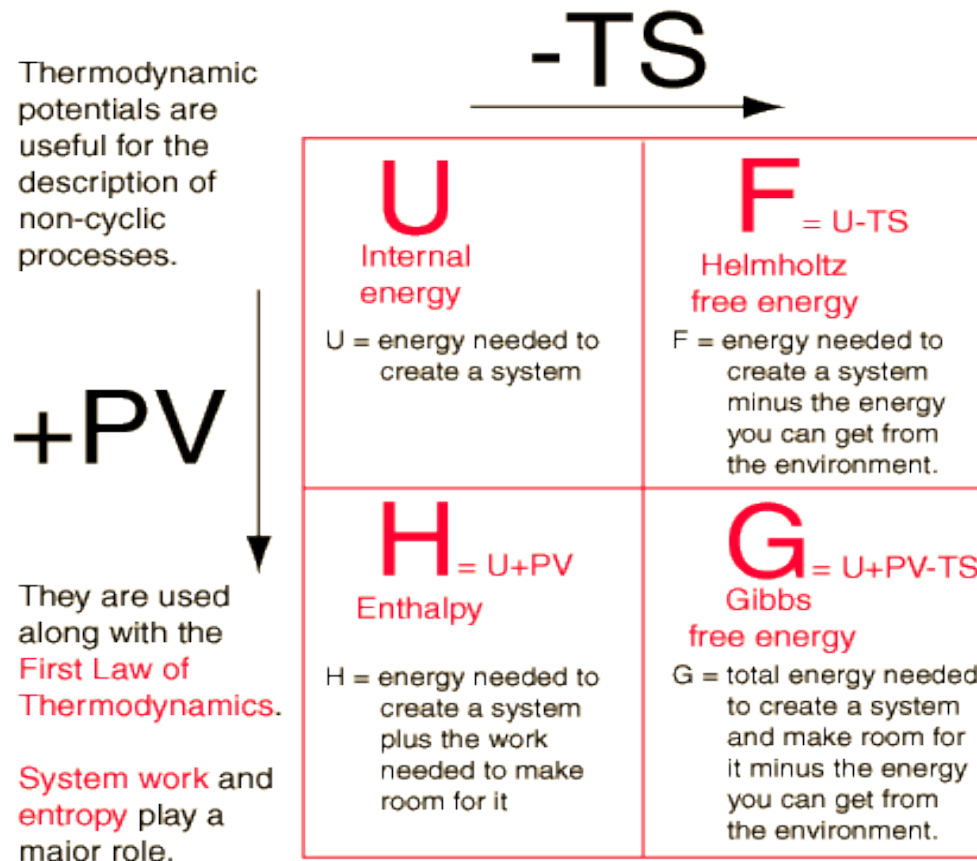


Figure 4.5 Relations of Thermodynamic potentials [8]

[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.