Advanced Thermodynamics (M2794.007900)

Chapter 4

Applications of the First Law

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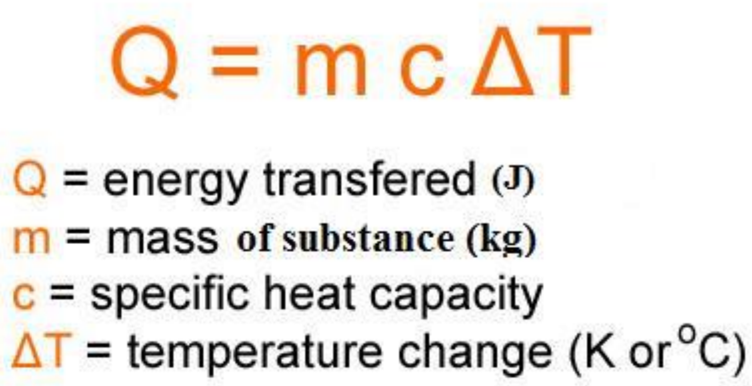
4.1 Heat Capacity

The heat capacity C

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

Specific heat capacity
=heat capacity per unit mass

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



$Q = m c \Delta T$

Q = energy transfered (J)
m = mass of substance (kg)
c = specific heat capacity
ΔT = temperature change (K or °C)

[1]

[1] https://thermalproperties.wikispaces.com/file/view/dd2.jpg/248898851/dd2.jpg

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

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

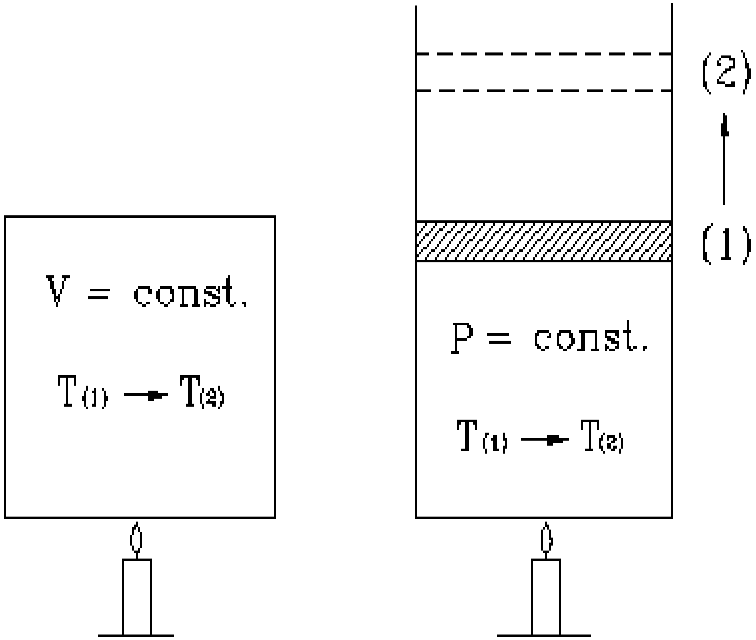


Figure Heat addition on different conditions [2]

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

4.1 Heat Capacity

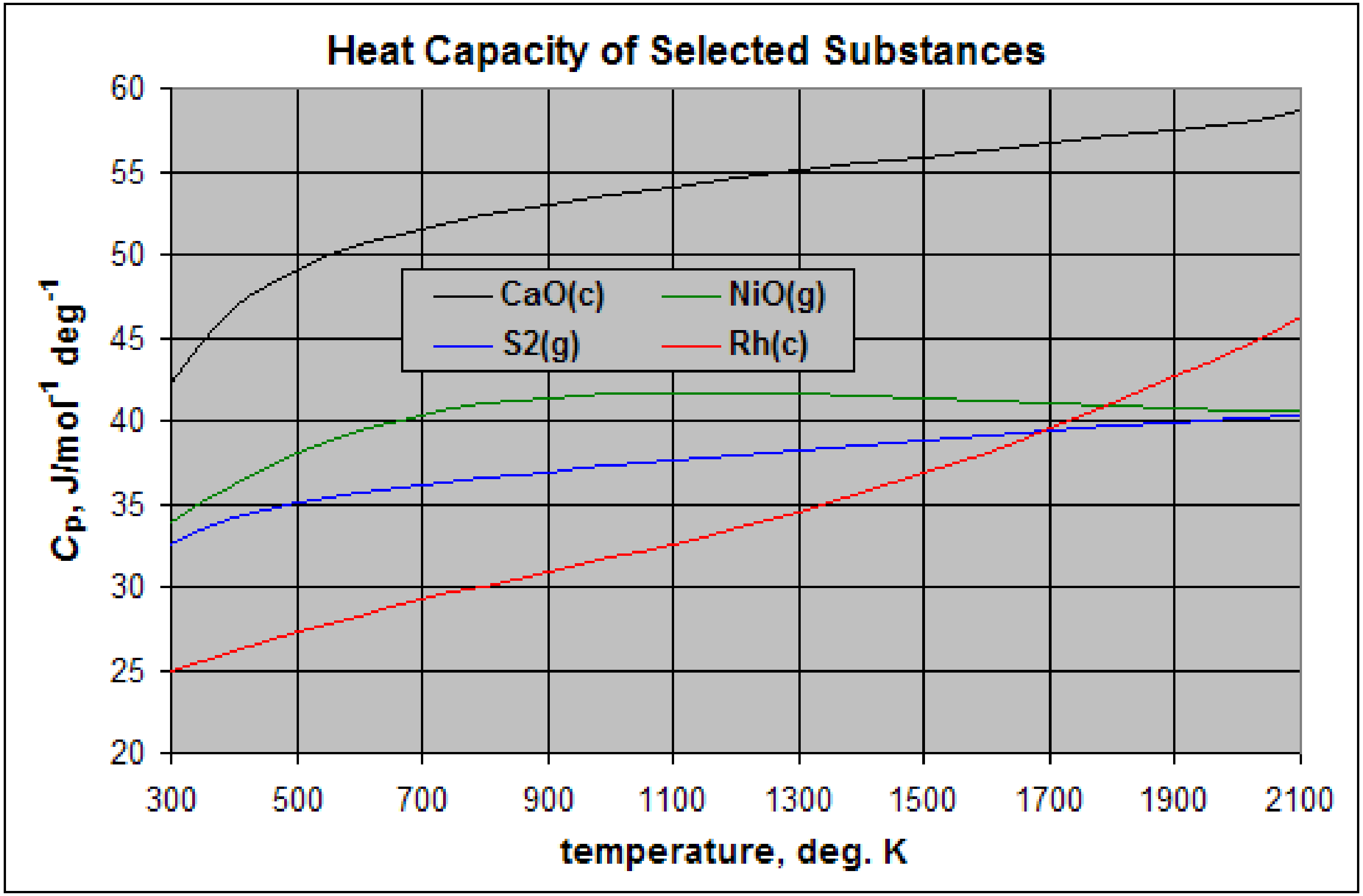


Figure Heat capacity of selected substances [3]

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

4.1 Heat Capacity

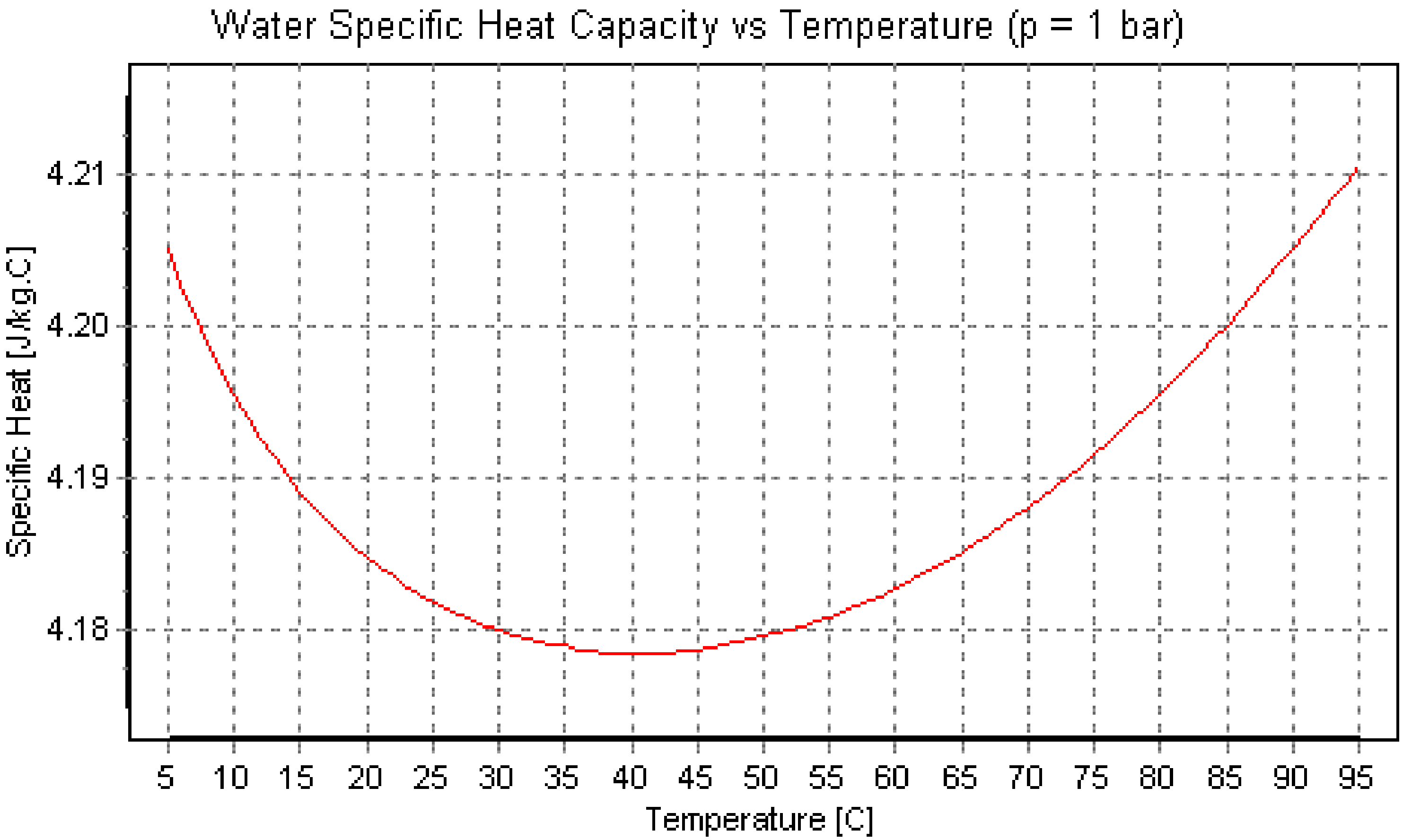


Figure Water Heat capacity [4]

[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

$$dU = \delta Q - PdV$$

$$du = \delta q - Pdv$$

$$u = u(v, T)$$

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

$$\delta q = c_v dT + Pdv$$

$$Pdv + vdP = RdT$$

$$\delta q = (c_v + R)dT - vdP$$

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

$\therefore c_p = c_v + R$ **This relation is known as Mayer's equation**

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

4.3 Enthalpy and Heats of Transformation

Types of heat transfer

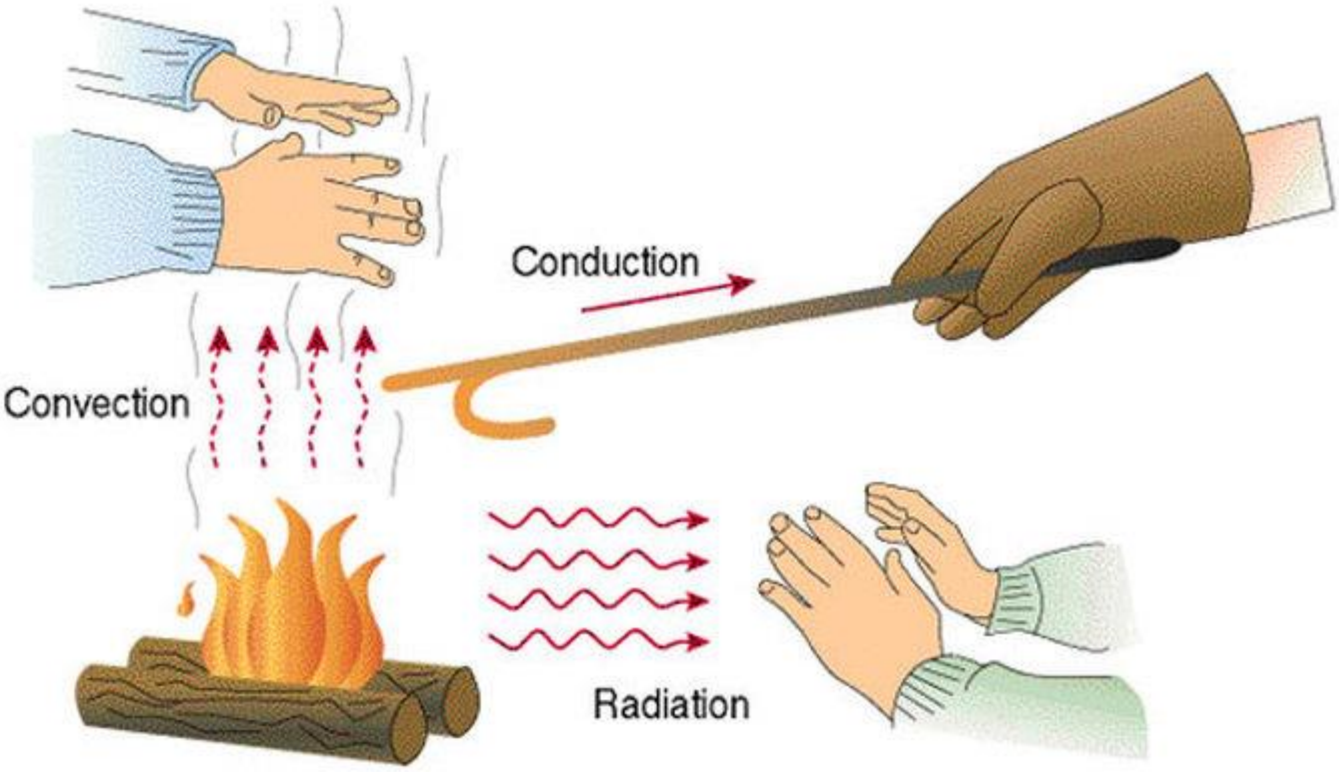


Figure Types of heat transfer [5]

[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

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.

So, $l = h_2 - h_1$

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

4.4 Relationships Involving Enthalpy

$$h = h(T, P)$$

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

$$h = u + Pv$$

$$dh = du + Pdv + vdP$$

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

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

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 $\delta q = c_p dT - vdP$

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

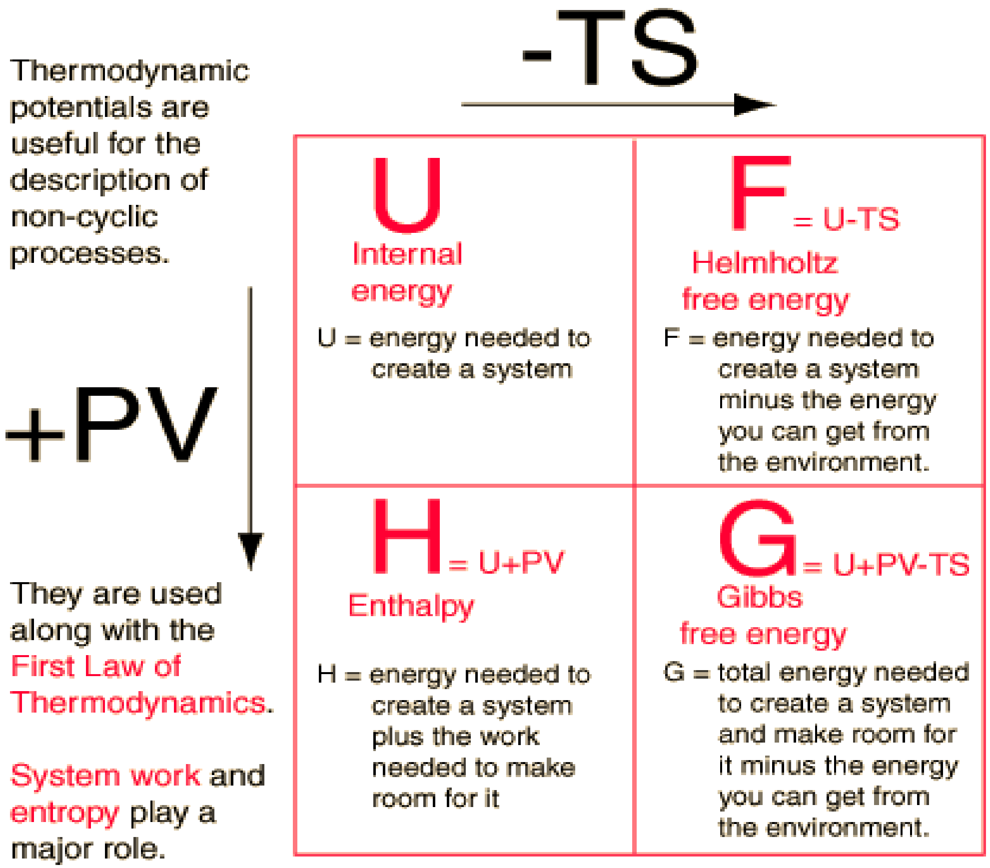
The parallel expressions involving the internal energy and the enthalpy

	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	$\delta q = c_v dT + Pdv$	$\delta q = c_p dT - vdP$
	$\left(\frac{\partial u}{\partial v}\right)_T = 0$	$\left(\frac{\partial h}{\partial P}\right)_T = 0$

Table Analogous relations involving the internal energy and the enthalpy

4.5 Comparison of u and h

Thermodynamic potentials: relations of the internal energy and the enthalpy



Thermodynamic potentials are useful for the description of non-cyclic processes.

They are used along with the First Law of Thermodynamics.

System work and entropy play a major role.

U

Internal energy

U = energy needed to create a system

F $= U-TS$

Helmholtz free energy

F = energy needed to create a system minus the energy you can get from the environment.

H $= U+PV$

Enthalpy

H = energy needed to create a system plus the work needed to make room for it

G $= U+PV-TS$

Gibbs free energy

G = total energy needed to create a system and make room for it minus the energy you can get from the environment.

Figure 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 $\delta q = c_p dT - vdP$, we obtain

$$vdP = c_p dT$$

We also have

$$\delta q = c_v dT + Pdv$$

Which for $\delta q = 0$ yields

$$Pdv = -c_v dT$$

$$\frac{vdP}{pdv} = -\frac{c_p}{c_v} = -\gamma \qquad \text{or} \qquad \frac{dP}{P} = -\gamma \frac{dv}{v}$$

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=constant)

The work done in the adiabatic process is

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

4.6 Work Done in an Adiabatic Process

Now, $K = Pv^{\gamma}$ at both limits: if we use $\mathrm{K} = P_2 {v_2}^{\gamma}$ at the upper limit and $\mathrm{K} = P_1 {v_1}^{\gamma}$ at the lower limit, we obtain

$$w = \frac{1}{1-\gamma}[P_2 v_2 - P_1 v_1]$$

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.