Chapter 4

Applications of the First Law

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4.1 Heat Capacity

The heat capacity C

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

Specific heat capacity = heat capacity per unit mass

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

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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

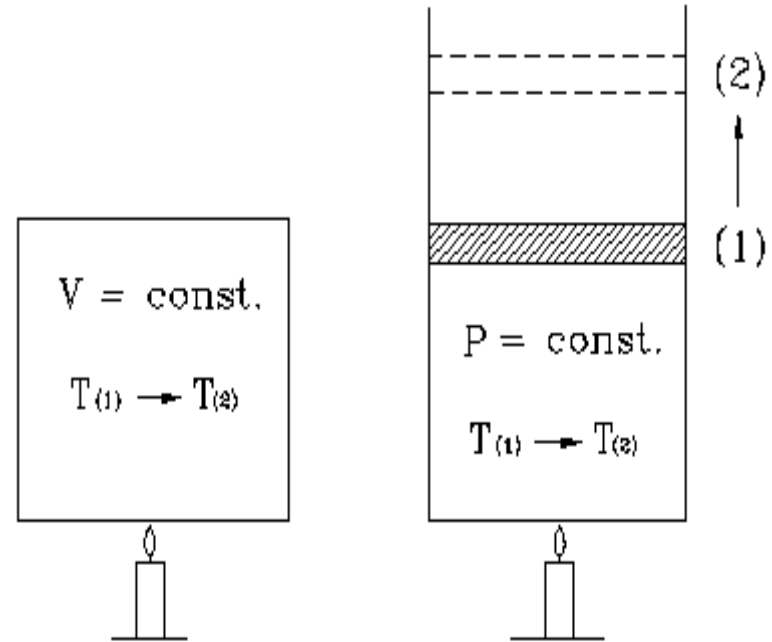$$c_p = \left(\frac{\delta Q}{dT}\right)_p$$

V = const.

T(1) ⟶ T(2)

P = const.

T(1) ⟶ T(2)

(2)

(1)

Figure 4.1 Heat addition on different conditions [2]

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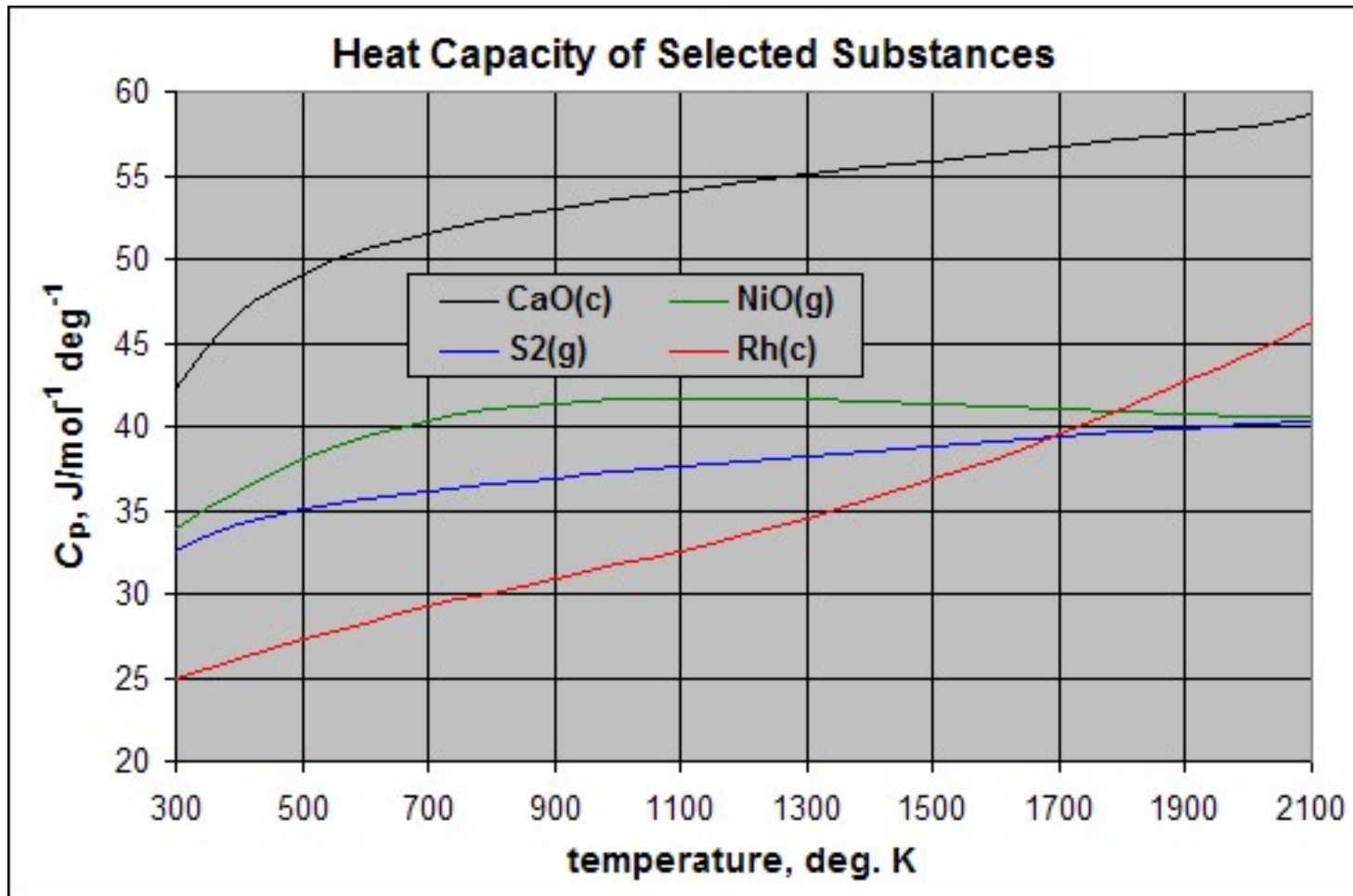
4.1 Heat Capacity

Figure 4.2 Heat capacity of selected substances [3]

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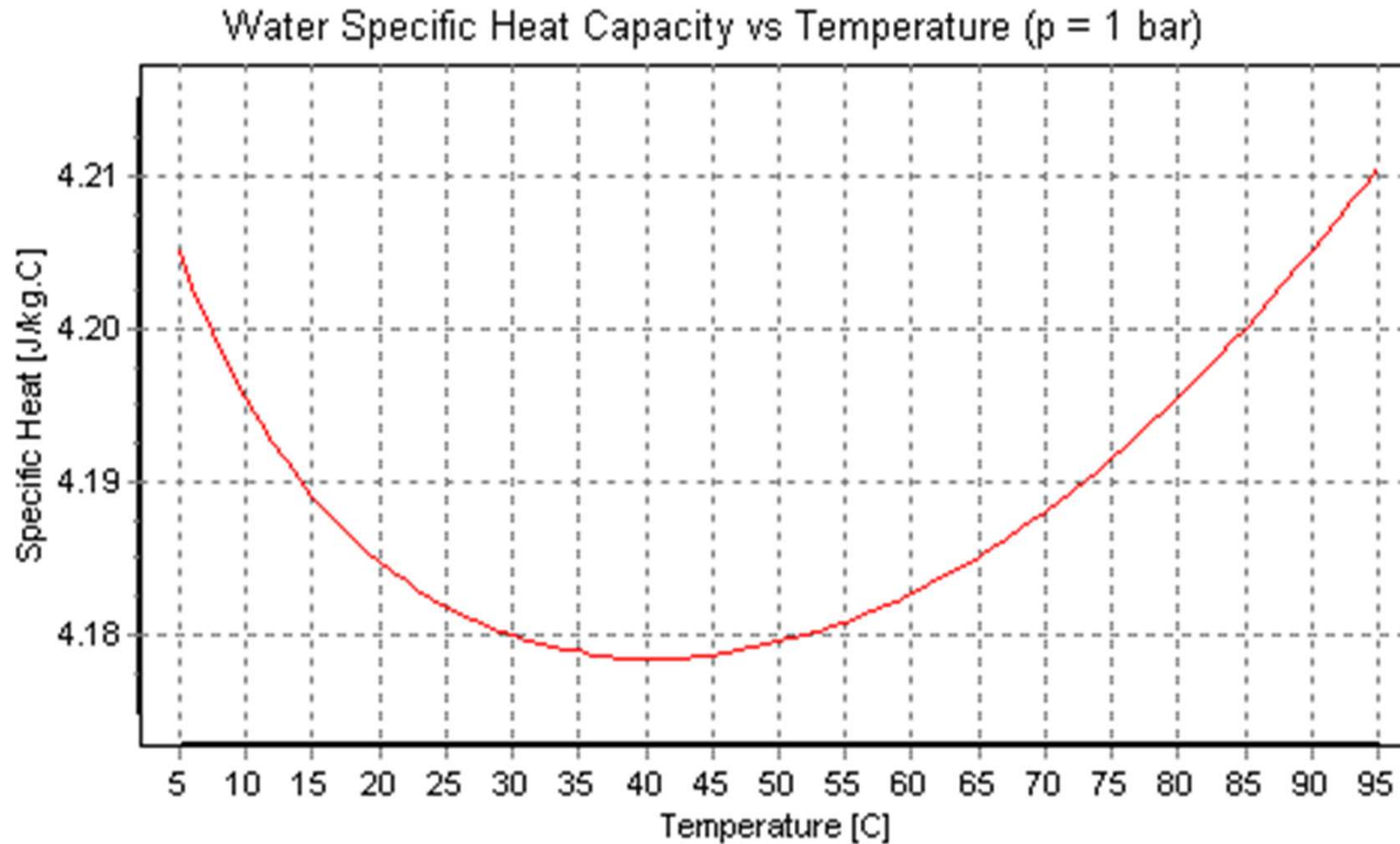
4.1 Heat Capacity

Figure 4.3 Water Heat capacity [4]

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

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

$$dU = \delta Q - PdV$$

$$du = \delta q - Pdv$$

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

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

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

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

$$Pdv + vdP = RdT$$

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

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

$$\therefore c_p = c_v + R \qquad \textbf{Mayer's equation}$$

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

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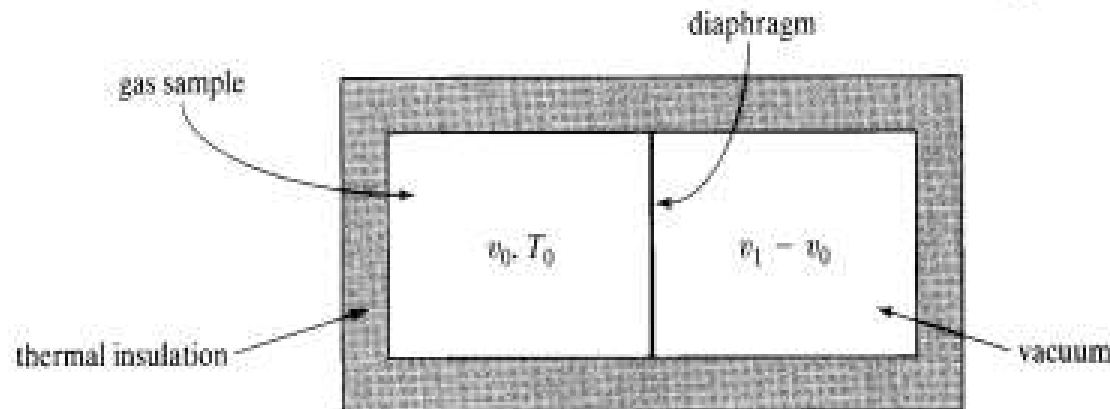
The heat of transformation is the heat transfer accompanying a phase change. A change of phase is an isothermal and isobaric process and entails a change of volume, so work is always done on or by a system in a phase change.

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

$$du = \delta q - Pdv$$

Or, for a finite change, $(u_2 - u_1) = l - P(v_2 - v_1)$
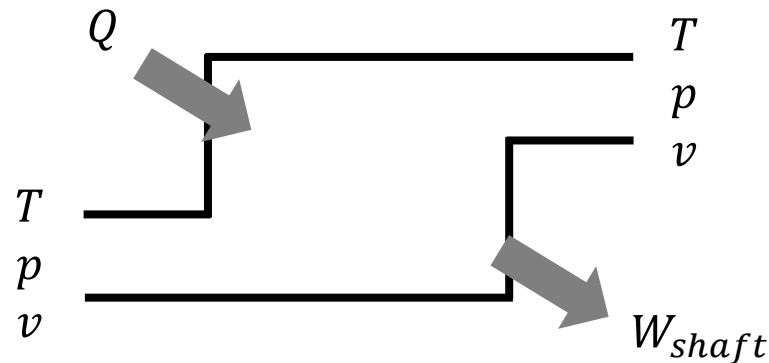
$$l = (u_2 + Pv_2) - (u_1 + Pv_1)$$

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

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

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

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

Q $\qquad$ T
p
v

T
p
v $\qquad$ W_{shaft}

∴ **The latent heat of transformation is equal to the difference in enthalpies of the two phases.**

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

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

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

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

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

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

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 $\qquad\qquad\qquad\qquad \delta q = c_p dT - vdP$

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

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 $P_1 \neq P_2$.
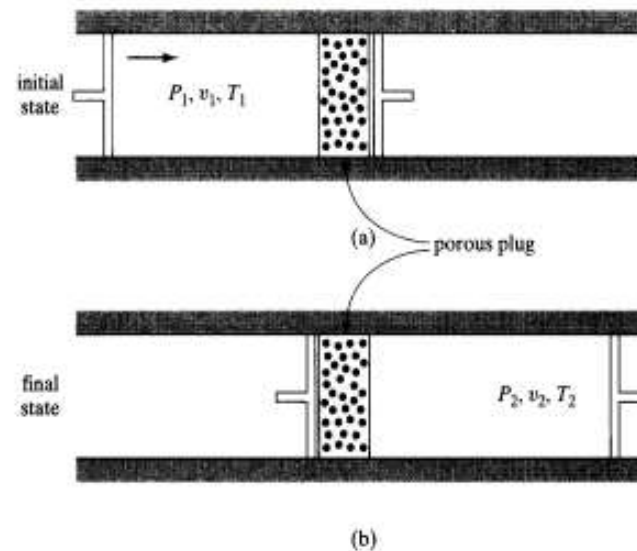
The parallel expressions involving the internal energy and the enthalpy

Table Analogous relations involving the internal energy and the enthalpy

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

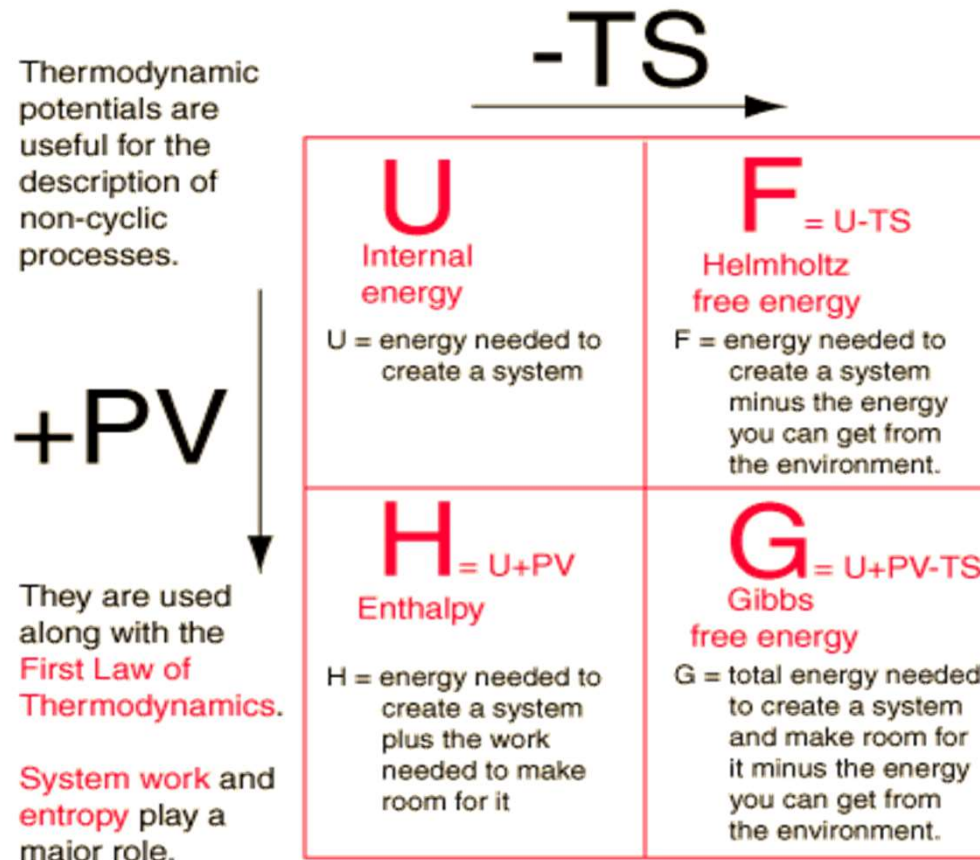**Thermodynamic potentials: relations of the internal energy and the enthalpy**

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

$$P dv = -c_v dT$$

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

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

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

4.6 Work Done in an Adiabatic Process

Now, $K = Pv^\gamma$ at both limits; if we use $K = P_2 v_2^\gamma$ at the upper limit and $K = P_1 v_1^\gamma$ 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.