# FIRST LAW OF THERMODYNAMICS: CONSERVATION OF ENERGY

I.   First Law of Thermodynamics *(VW, S & B: 2.6)*

A. <u>There exists for every system a property called energy</u>. **E = internal energy (arising from molecular motion - primarily a function of temperature) + kinetic energy + potential energy + chemical energy.**

1. Defines a useful property called "energy".

2. The two new terms in the equation (compared to what you have seen in physics and dynamics, for example) are the internal energy and the chemical energy. For most situtations in this class, we will neglect the chemical energy.

3. Let's focus on the internal energy, u. It is associated with the random or disorganized motion of the particles.

T₁ (molecular motion)   add heat →   T₂ (molecular motion)
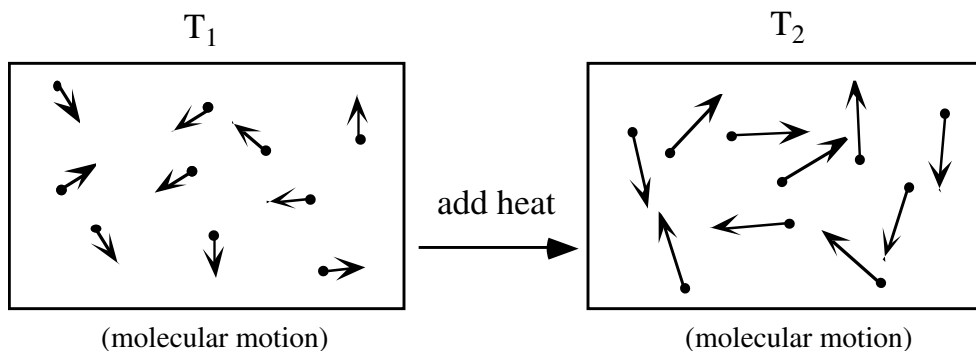
u is a function of the state of the system. Thus u = u (p, T), or u = u (p, v), or u = u(v,T). Recall that for pure substances the entire state of the system is specified if any <u>two</u> properties are specified. We will discuss the equations that relate the internal energy to these other variables later in the class.

B. The change in energy of a system is equal to the difference between the heat *added to* the system and the work *done by* the system. (This tells what the property energy is useful for.) *(VW, S & B: Chapter 5)*

$$\Delta E = Q - W \qquad \text{(units are Joules)}$$

1. The signs are important (and sometimes confusing!)

   E is the energy of the system
   Q is the heat transferred to the system (positive) - if it is transferred
   from the system Q is negative. *(VW, S & B: 4.7-4.8)*
   W is the work done by the system (positive) - if work is done on
   the system W is negative. *(VW, S & B: 4.1-4.4)*

2. The equation can also be written on a per unit mass basis

   $$\Delta e = q - w \qquad \text{(units are J/kg)}$$

3. In many situations the potential energy and the kinetic energy of the system
   are constant.

   Then $\Delta e = \Delta u$, and

   $$\Delta u = q - w \qquad \text{or} \qquad \Delta U = Q - W$$

   Q and W are path dependent, U is not it depends only on the state of the
   system, not how the system got to that state.

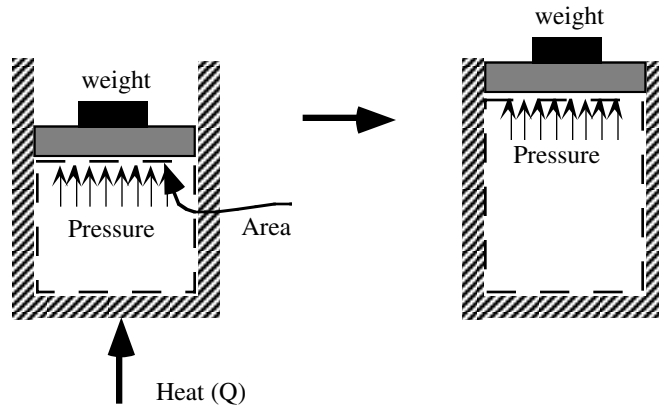4. Can also write the first law in differential form:

   $$dU = \delta Q - \delta W \quad \text{or} \qquad du = \delta q - \delta w$$

   Here the symbol "δ" is used to denote that these are not exact differentials but
   are dependent on path.

5. Or for quasi-static processes

   $$dU = \delta Q - pdV \qquad \text{or} \qquad du = \delta q - pdv$$

6. Example: Heat a gas, it expands against a weight. Force (pressure times area)
   is applied over a distance, work is done.

7. We will see later that the First Law can be written for a control volume with steady mass flow in and steady mass flow out (like a jet engine for example). We will call this the Steady-Flow Energy Equation. *(VW, S & B: 5.8-5.12)*

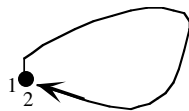8. We will spend most of the course dealing with various applications of the first law - in one form or another.

II. Corollaries of the First Law

A. Work done in any adiabatic (Q=0) process is path independent.

$$\Delta U = \cancel{Q}^{0} - W$$
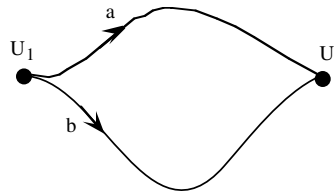
B. 2. For a cyclic process heat and work transfers are numerically equal

$U_{final} = U_{initial}$ therefore $\Delta U = 0$

and $Q = W$

or $\oint \delta Q = \oint \delta W$

III. Example applications of the First Law to motivate the use of a <u>property called "enthalpy"</u> *(VW, S & B: 5.4-5.5)*

A. The combination u+pv shows up frequently so we give it a name: "enthalpy"   h= u+pv (or H = U+pV). It is a function of the state of the system.

The utility and physical significance of enthalpy will be clearer when we discuss the steady flow energy equation in a few lectures. For now, you may wish to think of it as follows (Levenspiel, 1996). When you evaluate the energy of an object of volume V, you have to remember that the object had to push the surroundings out of the way to make room for itself. With pressure p on the object, the work required to make a place for itself is pV. This is so with any object or system, and this work may not be negligible. (Recall, the force of one atmosphere pressure on one square meter is equivalent to the force of a mass of about 10 tons.) Thus the total energy of a body is its internal energy plus the extra energy it is credited with by having a volume V at pressure p. We call this total energy the enthalpy, H.

B. Consider a quasi-static process of constant pressure expansion

$$Q = (U_2 - U_1) + W$$
$$= (U_2 - U_1) + p(V_2 - V_1) \qquad \text{since } p_1 = p_2 = p$$

so $\qquad Q = (U_2 + pV_2) - (U_1 + pV_1) = H_2 - H_1$

C. Consider adiabatic throttling of a gas (gas passes through a flow resistance). What is the relation between conditions before and after the resistance?
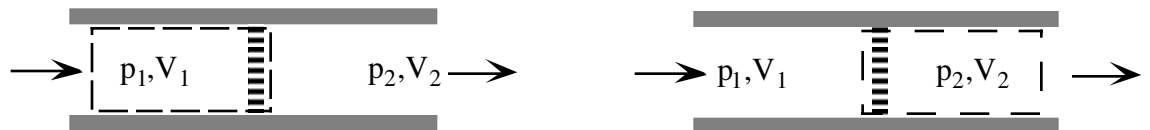
$Q = 0 \qquad$ therefore $\Delta U = - \Delta W$

or $\qquad U_2 - U_1 = -(p_2 V_2 - p_1 V_1)$

so $\qquad U_2 + p_2 V_2 = U_1 + p_1 V_1$

$H_2 = H_1$

IV. First Law in terms of enthalpy

$dU = \delta Q - \delta W$ (for any process, neglecting ΔKE and ΔPE)

$dU = \delta Q - pdV$ (for any quasi-static process, no ΔKE or ΔPE)

$H = U + pV$ therefore $dH = dU + pdV + Vdp$

so $dH = \delta Q - \delta W + pdV + Vdp$ (any process)

or

$\boxed{dH = \delta Q + Vdp \text{ (for any quasi-static process)}}$

V. Specific Heats and Heat Capacity *(VW, S & B: 5.6)*

A. <u>Question</u>**: Throw an object from the top tier of the lecture hall to the front of the room. Estimate how much the temperature of the room has changed as a result. Start by listing what information you need to solve this problem.**

B. How much does a given amount of heat transfer change the temperature of a substance? It depends on the substance. In general

$$Q = C\Delta T$$

where C is a constant that depends on the substance.

1. For a constant pressure process

$$C_p = \left(\frac{\delta Q}{\partial T}\right)_p \qquad \text{or} \qquad c_p = \left(\frac{\delta q}{\partial T}\right)_p$$

and for a constant volume process

$$C_v = \left(\frac{\delta Q}{\partial T}\right)_v \qquad \text{or} \qquad c_v = \left(\frac{\delta q}{\partial T}\right)_v$$

we use c_p and c_v to relate u and h to the temperature for an ideal gas.

2. <u>Expressions for u and h.</u> Remember that if we specify any two properties of the system, then the state of the system is fully specified. In other words we can write $u = u(T,v)$, $u=u(p,v)$ or $u=u(p,T)$ -- the same holds true for h. *(VW, S & B: 5.7)*

Consider a constant volume process and write $u = u(T,v)$. Then

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

where the last term is zero since there is no change in volume. Now if we write the First Law for a quasi-static process

$$du = \delta q - pdv$$

where again the last term is zero since there is no volume change. So

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

so

$$c_v \;=\; \left(\frac{\partial u}{\partial T}\right)_v$$

If we write h=h(T,p), and consider a constant pressure process, we can perform similar manipulations and show that

$$c_p \;=\; \left(\frac{\partial h}{\partial T}\right)_p$$

c_p and c_v are thermodynamic properties of a substance. The previous two relationships are <u>valid at any point in any quasi-static process</u> whether that process is constant volume, constant pressure, or neither.

C. Ideal gas assumption *(VW, S & B: 5.7)*

If we have a thermally perfect gas (i.e. it obeys pv=RT), then it is called an *ideal gas* if u = u(T) <u>only</u>, and h= h(T) <u>only</u>. Then

$$du \;=\; \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T^{\;0} dv$$

and

$$dh \;=\; \left(\frac{\partial h}{\partial T}\right)_p dT + \left(\frac{\partial h}{\partial p}\right)_T^{\;0} dp$$

so for an ideal gas

$$\boxed{du = c_v dT \qquad \text{and} \qquad \Delta u_{1-2} = \int_{T_1}^{T_2} c_v(T) dT}$$

and

$$dh = c_p dT \qquad \text{and} \qquad \Delta h_{1-2} = \int_{T_1}^{T_2} c_p(T)dT$$

Over small temperature changes ($\Delta T \approx 200K$), it is often assumed that c_v and c_p are constant.

D. First Law Expressions for an Ideal Gas

1. For an ideal gas undergoing a quasi-static process:

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

or in terms of enthalpy

$$\delta q = c_p dT - vdp$$

2. Relationships between thermodynamic properties c_v, c_p, and R

   a) Equating the two first law expressions given above

   $$c_p dT - vdp = c_v dT + pdv$$

   $$(c_p - c_v)dT = d(pv)$$

   $$c_p - c_v = d(pv)/dT \qquad \text{and} \quad pv = RT$$

   so
   $$c_p - c_v = R$$

   b) The ratio of specific heats, γ

   $$\gamma = c_p/c_v$$

3. Example: Quasi-static, adiabatic process for an ideal gas

$$\cancel{\delta q}^{\;0} = c_v dT + pdv \quad \text{and} \quad \cancel{\delta q}^{\;0} = c_p dT - vdp$$

   so
   $$c_v\, dT = -pdv \quad \text{and} \quad c_p\, dT = vdp$$

   therefore

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

   then

$$\gamma \ln \frac{v_2}{v_1} + \ln \frac{p_2}{p_1} = 0$$

or

$$\frac{p_2 v_2{}^{\gamma}}{p_1 v_1{}^{\gamma}} = 1$$

finally, we arrive at the very useful expression

$$pv^{\gamma} = \text{constant}$$

from which it can also be shown that

$$\frac{p_2}{p_1} = \left(\frac{T_2}{T_1}\right)^{\gamma/\gamma-1} \qquad \text{and} \qquad \frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$$

We will use the above equation to relate pressure and temperature to one another for quasi-static adiabatic processes (our idealization of what happens in compressors and turbines).

E. Questions:

1. On a p-v diagram for a closed-system sketch the thermodynamic paths that the system would follow if expanding from volume = v_1 to volume = v_2 by isothermal and quasi-static, adiabatic processes.

2. For which process is the most work done by the system?

3. For which process is there heat exchange?   Is it added or removed?

4. Is the final state of the system the same after each process?

5. Derive expressions for the work done by the system for each process.