FIRST LAW OF THERMODYNAMICS: CONSERVATION OF ENERGY

1. **First Law of Thermodynamics** 
   1. There exists for every system a property called energy. **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 T2



add heat

(molecular motion) (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 two properties are specified. We will discuss the equations that relate the internal energy to these other variables later in the class.

* 1. 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)*

E = Q - W (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)*

* + 1. The equation can also be written on a per unit mass basis

e = q - w (units are J/kg)

* + 1. In many situations the potential energy and the kinetic energy of the system are constant.

Then e = u, and

u = q - w or 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.

* + 1. Can also write the first law in differential form:

dU = Q - W or du = q - w

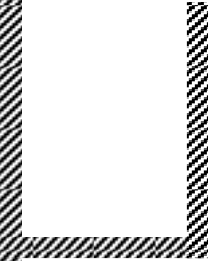
Here the symbol “” is used to denote that these are not exact differentials but are dependent on path.

* + 1. Or for quasi-static processes

dU = Q - pdV or du = q - pdv

* + 1. Example: Heat a gas, it expands against a weight. Force (pressure times area) is applied over a distance, work is done.

weight

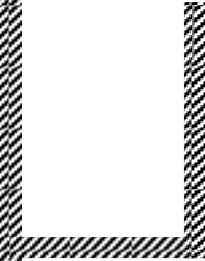


weight

Pressure

Area

Heat (Q)



Pressure

* + 1. 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)*
    2. We will spend most of the course dealing with various applications of the first law - in one form or another.

1. Corollaries of the First Law
   1. Work done in any adiabatic (Q=0) process is path independent.

0



a

U1

U2

b



Q

U = - W

* 1. 2. For a cyclic process heat and work transfers are numerically equal

Ufinal = Uinitial therefore U = 0 and Q = W

1 2

or  Q   W

1. Example applications of the First Law to motivate the use of a property called “enthalpy”



p1,V1

p2,V2

* 1. 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.

* 1. Consider a quasi-static process of constant pressure expansion

Q = (U2 - U1) +W

= (U2 - U1) + p(V2 - V1) since p1 = p2 = p so Q = (U2 + pV2) - (U1 + pV1) = H2 - H1

* 1. Consider adiabatic throttling of a gas (gas passes through a flow resistance). What is the relation between conditions before and after the resistance?



p1,V1

p2,V2

Q = 0 therefore U = - W or U2 - U1 = -(p2V2 - p1V1)

so U2 + p2V2 = U1 + p1V1

H2 = H1

1. First Law in terms of enthalpy

dU = Q - W (for any process, neglecting KE and PE) dU = Q - pdV (for any quasi-static process, no KE or PE)

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

so dH = Q - W + pdV + Vdp (any process) or

dH = Q + Vdp (for any quasi-static process)

1. **Specific Heats and Heat Capacity *(VW, S & B: 5.6)***
   1. Question: 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.
   2. **How much does a given amount of heat transfer change the temperature of a substance? It depends on the substance. In general**

Q = CT

where C is a constant that depends on the substance.

* + 1. For a constant pressure process

Cp

  Q

 T  p

or cp

  q 

 T p

and for a constant volume process

C   Q

v  T  v

or cv

  q 

 T v

we use cp and cv to relate u and h to the temperature for an ideal gas.

* + 1. Expressions for u and h. 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 

 u 

 T v

dT   u dv

 v T

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 = q - pdv

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

q 

so

 u 

 T

dT so

v

 u 

 T v

  q 

 T v

 cv

cv 

 u 

 T v

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

cp 

 h 

 T p

cp and cv are thermodynamic properties of a substance. The previous two relationships are valid at any point in any quasi-static process whether that process is constant volume, constant pressure, or neither.

* 1. **Ideal gas assumption**

If we have a thermally perfect gas (i.e. it obeys pv=RT), then it is called an

*ideal gas* if u = u(T) only, and h= h(T) only. Then

0

and

so for an ideal gas

du 

dh 

 u 

 T v

 h 

 T p

dT   u dv

 v T

0

dT   h  dp

 p T

du  cvdT

T 2

and u1 2   cv (T)dT

T1

and

dh  cpdT

T 2

and h1 2   cp (T)dT

T1

Over small temperature changes (T  200K), it is often assumed that cv and cp are constant.

* 1. First Law Expressions for an Ideal Gas
     1. For an ideal gas undergoing a quasi-static process:

q = cvdT + pdv

or in terms of enthalpy

q = cpdT - vdp

* + 1. Relationships between thermodynamic properties cv, cp, and R
       1. Equating the two first law expressions given above

cpdT - vdp = cvdT + pdv (cp - cv)dT = d(pv)

cp - cv = d(pv)/dT and pv = RT

so

cp - cv = R

* + - 1. The ratio of specific heats, 

 = cp/cv

* + 1. Example: Quasi-static, adiabatic process for an ideal gas

0 0



q

q = cvdT + pdv and

so

= cpdT - vdp

cv dT = -pdv and cp dT = vdp therefore

cp   v dp

or  dv   dp

cv

then

p dv v p

 ln v2

v1

or

* ln p2  0 p1

p2 v2   1 p1v1

finally, we arrive at the very useful expression pv = constant

from which it can also be shown that

p  T 



 1

T  v   1

p1

2   2 

 T1 

and

T1

2   1 

 v2 

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).

* 1. Questions:
     1. On a p-v diagram for a closed-system sketch the thermodynamic paths that the system would follow if expanding from volume = v1 to volume = v2 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.