Thermodynamics
GENERAL
Lecture 3

Work, heat, the first law of thermodynamics
(Read pages 536-551 Physics for Scientists and Engineers (Third Edition) by Serway)

I. Work of expansion (W)
   A. Work is not a thermodynamic property (it is not an exact differential)
   B. If a system is not in mechanical equilibrium with its surroundings it can expand or contract so it is or it can move.
      1. Work is only done on boundaries of a system,
   C. An expanding gas does work on its surroundings (ΔW > 0).
   D. A contracting gas is worked upon by the surrounding (ΔW < 0).
   E. Work energy is defined as the energy associated with applying a force resulting in a change in a measure of distance (length, area, volume).
      1. There are other ways to represent work as in the previous lecture.
   F. Consider a piston where A is the cross-sectional area, V is the volume, and l is distance the piston moves, so dV = A dl, and
      \[ W = \int F \Sigma dl \]
      which is the integral of force (F) times displacement (dl).
         1. Pressure (p) = Force / Area (A); so \( F \cdot dl = pA \cdot dl \)
            a. \( dW = pA \cdot dl \)
            b. Work can be defined (for a reversible - frictionless - system) as
               \[ W = \int_{V_1}^{V_2} p \, dV \]
               You can compute the work done as the area under the curve defined by the equation above.
   G. We can take an initial look at work done in a cycle...(more later)
      a. For small \( dV \), we can assume for now a constant pressure.
      b. The work done in a cycle then can be said to be
         \[ W = \int_{V_1}^{V_2} p \, dV = \left( \int_{V_1}^{V_2} p \, dV \right) - \left( \int_{V_1}^{V_2} p \, dV \right) \]
   H. Work depends on the initial, intermediate, and final states. The sum total of work is path dependent. Work is not an exact differential. Draw a figure showing this.

II. First Law of Thermodynamics-Conservation of Energy
   A. Physical perspective
      1. Consider a body of molecules
         a. Three energies with body are
            i. macroscopic KE
            ii. macroscopic PE
            iii. microscopic U = (KE + PE of molecules; PE with molecular attractive forces between molecules).
b. Increases in U occur from
   i. Increases in KE due to increase in molecular speeds ---
      increase in temperature
   ii. Increases in PE due molecular / atomic configuration ---
      change in molecular separation distances

c. Assume that an infinitesimally small amount of heat dQ flows into
   some system with unit mass
   i. e.g., by radiation or conduction

d. The body now might do external work dW (e.g., expand)
   i. some of the heat dQ goes into work dW
      •Remember dQ and dW are path dependent (not exact
       differentials except in special cases)
   ii. dQ is positive when heat enters the system and dW is
      positive when work is done by the system
   ii. excess energy supplied to the body is dQ-dW

e. Assuming no change in macroscopic KE or PE, by conservation of
   energy (First Law of TD), U must increase if dQ - dW > 0
   i. dQ - dW = dU = U2-U1
   ii. U1 = initial internal energy,
      U2 = final internal energy

f. dQ - dW = dU
   i. dQ = differential increment of heat added to body
   ii. dW = differential work done by body
   iii. dU = differential increase in internal energy of body;
        independent of manner body changes;  dependent only on
        initial and final state

g. The work W can be written as (noting p = nR*T/V)
   \[ W = \int_{V_1}^{V_2} p \, dV = nR \int_{V_1}^{V_2} \frac{dT}{\ln V} \]

h. The First Law of TD can, thus, be written as
   \[ dQ = dU + pdV \]
   i. per unit mass...(\alpha = V/m)
   \[ dq = du + p\alpha \]

2. Joules' Law
   a. If an ideal gas expands into a vacuum without doing work (pdV=0),
      and dQ=0, then the temperature T of the gas will not change.
      i. dQ = dW = 0 so that by the First Law of TD that dU = 0.
      ii. This means temperature does not change and the mean
          kinetic energy does not change (is constant).
   b. From this we can determine the dependence of internal energy.
      i. We know the gas expanded --- the separation of the
         molecules increased. The part of U owing to molecular PE
         must be constant--in an ideal gas the molecules do not have
         intermolecular attractive forces. U does not depend on
         macroscopic PE.
   c. Conclusion: For an ideal gas, U depends only upon temperature.
3. Cyclic process.
   a. A cyclic process is one that starts and ends at the same state.
      i. The change in internal energy (an exact differential) will be zero \( (dU = 0) \)
      ii. \( dQ = dW \neq 0 \)
   b. As we said before the work done is the area under the curve in a \( p - V \) diagram, for example.
   c. If the work done is zero.
      i. \( dU = dQ; \) if heat enters the system \( (dQ > 0) \) \( U \) increases.
         • The increase in \( U \) corresponds to the increase in KE
   d. If heat transfer is zero, and work is done by the system, then \( dU = -dW \) so the value of \( U \) decreases. (Not true if macroscopic KE/PE are considered)
      i. Books example. Gas compressed in piston with no heat transfer.
         • Work is negative and \( U \) increases
         • KE is transferred from moving piston to gas molecules
   f. No difference of heat and work on microscale -- both can change internal energy
   g. On macroscale, \( Q \) and \( W \) are not "properties of a system".
      i. \( Q \) and \( W \) are related to \( U \) by the First law of thermodynamics.
      ii. Once path of process is defined,... \( Q \) and \( W \) can be calculated/measured.
   h. Crucial to remember that there is a quantity called internal energy defined by the state of the system--it is a state function--it is an exact differential.

3. Heat Capacity; Specific Heat, A little more.....
   a. Heat capacity (\( C \)) is the heat change per temperature change.
   b. Specific heat (\( c \)) is heat capacity / mass
      i. \( c_p = C_p/m \)
      ii. \( c_v = C_v/m \)
   c. The heat capacity of a substance depends on how the substance is heated.
   c. At constant volume, as heat is acquired, heat capacity \( C_v \) is
      i. \( dV = 0 \)
      ii. \( dq = du \)
      iii. \( c_v = dq/dT = du/dT \)
      iv. \( dq = c_v dT + dw: \) First Law
   d. At constant pressure, as heat is acquired, heat capacity \( C_p \) is
      i. \( c_p = dq/dT \)
      ii. \( dq = c_v dT + p d\alpha \\
          = c_v dT + d(p\alpha) - \alpha dp \\
          = c_v dT + R dT - \alpha dp \\
          = (c_v + R) dT - \alpha dp \)
      iii. \( dq = (c_v + R) dT; \) at constant pressure
      iv. \( c_p = c_v + R \)
      v. \( dq = c_p dT - \alpha dp \) (THIS IS NOT THE FIRST LAW)
e. Why is $cp > cv$
   i. Some of the heat goes into doing work of expansion in a constant $p$ process.
   ii. $cv = 717 \text{ J} / \text{ K} / \text{ kg}$
   iii. $cp = 1004 \text{ J} / \text{ K} / \text{ kg}$

III. Adiabatic processes
A. There is no heat exchange ($dq = 0$) between some substance and the environment of the substance in an adiabatic process.
   1. The work done by, for example, an expanding gas during an adiabatic transformation ($dq=0$) is
      a. $dq = 0 = du + dw = cvdT + dw$
      b. $dw = -cvdT$
      c. The work done is equal to the change (decrease) in internal energy.
         i. The energy to do the work is from internal energy of the gas.
      d. An adiabatically expanding gas does work, so $dU$ is negative, and temperature is negative.
   2. An air parcel is characterized by the following
      a. Thermally insulated from the environment
         i. Temperature changes in the air parcel are adiabatic during compression/expansion
         ii. Parcel pressure is same as environmental pressure at all levels
         iii. Parcels move slowly so that macroscopic kinetic energy is a negligible portion of total energy (IE and macroscopic PE)
   3. Variation of temperature under adiabatic conditions; $dq = 0$; and using the hydrostatic assumption.
      a. $dq = 0 = cp \,dT - 1/\rho \, dp$
      b. $cp \,dT = 1/\rho \, dp$
      c. $dp/\,dz = -g/\rho$ (hydrostatic equation)
      d. $cp \,dT = -g \, dz$
      e. $dT/\,dz = -g/cp = \Gamma d = 9.8^{\circ}/\text{km} \quad \text{(g=9.8 m s}^{-2})$
   4. Potential temperature - Definition and derivation
      a. The potential temperature is the temperature an air parcel would have if it were moved adiabatically to $p_o = 1000 \text{ mb}$ (the standard reference level and reference pressure $p_o$) or any reference pressure.
      b. $dq = 0 = cp \,dT - 1/\rho \, dp$
      c. $p = \rho RT; \quad 1/\rho = RT/p$
      d. $cp \,dT = 1/\rho \, dp$
      e. $cp \,dT = RT \,(dp/p)$
      f. $cp/R \,dT/T = dp/p$
    g. integrating from $p_o (T = \theta)$ to $p (T)$
       \[ \frac{c_p}{R} \int_{T_o}^{T} \frac{dT}{T} = \int_{p_o}^{p} \frac{dp}{p} \]
    h. $cp/R \ln(T/\theta) = \ln(p/po)$
    i. $\theta = T \,(p/po)^{(R/cp)}$
       i. Poisson's Equation
IV. Isobaric Processes. Enthalpy

A. Enthalpy is sometimes called the heat content added to a system.
   1. It is a useful measure of the heat accompanying, for example, chemical reactions.
   2. Enthalpy is a thermodynamic property, and a state function, and an exact differential.
   3. When applied to an isolated system enthalpy is related to the principle of conservation of energy.

B. To begin to understand enthalpy, consider the addition of heat to some substance
   1. Assume the heat is added at constant p
   2. The specific volume increases from $\alpha_1$ to $\alpha_2$

C. We now take a look at the First Law
   1. $dq = du + pd\alpha$
      $dq = (u_2 - u_1) + p(\alpha_2 - \alpha_1)$
      $dq = (u_2 + p\alpha_2) - (u_1 + p\alpha_1)$
      a. Subscript 1 is initial state and subscript 2 is final state

D. The quantity Enthalpy $h$ is defined as...
   1. $h = u + p\alpha$

E. Now, as we have a process at constant p
   $dq = h_2 - h_1 = dh$

F. For a constant pressure process in a system, the change in enthalpy is just the heat added to the system.
   1. So, for constant p
      a. $\alpha dp = 0$
      b. $dq = dh = cp dT$
      c. The change in the enthalpy of a system is the heat added to the system at constant pressure

G. We can differentiate $h = u + p\alpha$
   1. $dh = du + d(p\alpha)$
   2. $dh = du + pd\alpha + \alpha dp$
   3. Substituting the First Law ($dq = du + pd\alpha$; which is $du = dq - pd\alpha$)
   4. $dh = dq - pd\alpha + pd\alpha + \alpha dp = dq + \alpha dp$
   5. $dq = dh - \alpha dp$

H. Exothermic and Endothermic processes
   1. If $\Delta h < 0$; system is undergoing an exothermic change
      a. Heat in the system decreases
   1. If $\Delta h > 0$; system is undergoing an endothermic change
      a. Heat in the system increases

I. In summary, for heat absorbed by system in a reversible process at constant volume $dQ_v = du$. For a system with constant pressure, $dQ_p = dh$.

V. Isovolumetric process

A. If heat is added and volume is kept constant (work is zero) all heat goes to increasing the internal energy.
   1. $dU = dQ$
VI. Isothermal process.
A. As \( U \) is a function of only \( T \) in an ideal gas, \( dU = 0 \).
B. Isothermal expansion.
\[
W = \int_{v_i}^{v_f} p dV = nR T \int_{v_i}^{v_f} d\ln V = nR T \ln \left( \frac{V_f}{V_i} \right)
\]
1. If gas expands isothermally, \( V_f > V_i \).
   a. Work done by gas is positive
2. If gas compresses isothermally, \( V_f < V_i \)
   a. Work done by gas is negative

VII. Latent heat
A. A change in the physical state of a substance (at constant \( T \)) may occur by
   absorption of heat at constant pressure. (e.g., the heat required to change a mass of,
   for example, liquid to vapor, at constant \( p \) and \( T \).
1. The heat absorbed by a substance is
   \[
   dQ = L dm
   \]
   a. \( Q \) is heat
   b. \( L \) is latent heat of the substance
   c. \( dm \) is the change in mass (due to change in physical state)
2. The heat absorbed is used changing the molecular configuration

B. In general, latent heat is defined for a phase change at constant pressure.
1. We can think of latent heat in terms of Enthalpy
   a. \( L = \Delta H \quad (l = \Delta h) \)
2. We need to know how \( L \) varies as temperature varies.
   a. We start with realizing \( H \Rightarrow H(T,p) \); so
   \[
   \Delta H = \partial H/\partial T \ dT + \partial H/\partial p \ dp
   \]
   b. Now, consider an initial state 1 and a final state 2 so \( \Delta H = H_2 - H_1 \)
   c. Taking the difference of the differentials \( dH_1 \) and \( dH_2 \)
   \[
   (dH_2-dH_1) = \partial(\Delta H)/\partial T \ dT + \partial(\Delta H)/\partial p \ dp
   \]
   d. With \( p \) = constant, we now define how \( L \) changes with \( T \)
   \[
   dL = d(\Delta H) = \partial(\Delta H)/\partial T \ dT = \partial(H_2)/\partial T \ dT - \partial(H_2)/\partial T \ dT
   = (cp_2 - cp_1) \ dT
   \]
   i. We defined above that \( dh/dT = cp \) for constant pressure process
   e. So, we can say \( \partial L/\partial T = \Delta(cp) \)
   i. For a constant pressure process
   ii. Called Kirchoff’s Equation
   iii. This can be stated as;
   'L varies with T as the difference between heat capacities
   between the two phases involved' for constant pressure process
C. Latent heat for water (approximate – there are new estimates now available)
   1. Latent Heat of Fusion: (solid -> liquid; or liquid -> solid)
      a. \( L_f = 3.34 \times 10^5 \text{ J kg}^{-1} \)
      b. \( L_f = 333,690 + 2030.6 (T-273.15) -10.467(T-273.15)^2 \)
   2. Latent Heat of Vaporization: (vapor -> liquid; or liquid -> vapor)
      a. \( L_v = 2.5 \times 10^6 \text{ J kg}^{-1} \) (0°C)
      b. \( L_v = 2.25 \times 10^6 \text{ J kg}^{-1} \) (100°C)
      c. \( L_v = 2,500,780 \frac{273.15}{T} x = 0.167 + 0.000367T \)
   3. Latent Heat of Sublimation (vapor -> solid; or solid -> vapor)
      a. \( L_s = L_v + L_f = 2.834 \times 10^6 \text{ J kg}^{-1} \)

VIII. Heat transfer (543-551)
   A. The concepts associated with heat transfer that are important to understand are
      1. rate that heat is transferred
      2. the physical mechanism of heat transfer
   B. Heat conduction
      1. Heat conduction is the best understood as a transfer of kinetic energy on the atomic scale from one molecule to another molecule by collision or direct contact.
      2. Less energetic molecules gain energy by colliding with more energetic ones and visa versa.
         a. atomic vibration and electron motion are essential to heat conduction especially in solids in liquids
      3. Heat conduction also depends on characteristics of substance being heated.
         a. asbestos heats at a much different rate than iron
         b. in general
            i) metals are good heat conductors as they have many molecules and electrons which are free to move through the metal
            ii) asbestos, cork, paper, fiber glass are poor conductors
            iii) gases are poor conductors owing to their dilute nature
      4. Heat conduction only occurs when there is a temperature difference between two parts of a conducting medium
         a. Heat flows from warm to cold
         b. If \( T_2 > T_1 \), heat flow across a slab of thickness \( dx \) is \( \frac{dQ}{dt} \) proportional to \( A \frac{dT}{dx} \)
            i. \( A \) is the cross-sectional area of the slab
            ii. \( H = \frac{dQ}{dt} = \text{heat transfer rate and has units of watts} \) (1W = 1J/s)
c. Law of heat conduction
\[ H = -kA \frac{dT}{dx} \]
\[ k \] is thermal conductivity \((\text{W m}^{-1} \text{K}^{-1})\):
- Good conductors have large thermal conductivities
  - gold = 314
  - lead = 34.7
  - iron = 79.5
  - air = 0.0234
  - asbestos = 0.08
  - concrete = 0.8
  - water = 0.6 \(\text{(ice}=2)\)
  - wood = 0.08

ii. For steady state heat transfer
\[ \frac{dT}{dx} = \frac{(T_1 - T_2)}{L} \text{ amd} \]
\[ H = kA \frac{(T_2 - T_1)}{L} \]

d. Heat transfer through multiple slabs in contact with each other
\[ H = A \frac{(T_2 - T_1)}{\sum (Li/ki)} \]

C. Convection
1. Convection describes heat transfer by movement of a heated substance
   a. When heat transfer occurs in this manner owes it owes to differences in density, it is called natural convection
   b. When heat transfer is by an external force (fan, pump), then it is called forced convection
   c. Example: a u shaped tube with water in it
      i. In case a) the temperature of the water is the same and thus the water level stays equal on both sides.
      ii. In case b) assume one side of the tube has cold water and the other hot water owing to it being heated and the stopcock is closed.
         • The water on the heated side expands, and thus has lower density
         • A longer tube is needed to balance the pressures
         • Now open the stopcock, and water will flow from the top of the warm column into the cold side.
         • This further increases the pressure at the bottom of the cold side and decreases the pressure on the warm side.
         • At the bottom of the tube, water is forced from the cold to the warm side owing to density differences.
         • If heat is continually applied to the right side the process continues (the old fashioned household hot water heating system).

2. The mathematical theory of convection for gases and fluids is complex and not covered in this class. There are many issues related to the many factors when heat is lost or gained from a surface in contact with a fluid at a different temperature. These factors include:
   a. whether surface is flat or curved
   b. whether surface is horizontal or vertical
   c. whether fluid is in contact with the surface is a gas or liquid
d. the density, viscosity, specific heat, and thermal conductivity of the fluid.
e. whether the velocity of the fluid is small enough to give rise to laminar flow or large enough to cause turbulent flow.
f. whether evaporation, condensation, or formation of scale takes place.
g. A system of equations used to study fluid dynamics are:
   • momentum: $\frac{\partial u_i}{\partial t} = - u_j \frac{\partial u_i}{\partial x_j} - \frac{\partial p}{\partial x_i} - g_k + F_i$
   • energy: $\frac{\partial \theta}{\partial t} = - u_j \frac{\partial \theta}{\partial x_j} + F_\theta$
   • continuity: $\frac{\partial \rho}{\partial t} = \frac{\partial \rho u_i}{\partial x_i}$
   • state: $P = \rho R T$

D. Radiation
1. First it is important to remember that all objects radiate energy in the form of EM waves.
2. Radiation associated with heat transfer is called infrared radiation
3. Stefan's law describes the rate at which an object emits radiant energy and shows it to be proportional to the fourth power of its absolute temperature
   $$P = \sigma A e T^4$$
   a. $P =$ power radiated (W or J/s)
   b. $\sigma =$ constant equal to $5.6696 \times 10^{-8}$ W K$^{-4}$ m$^{-2}$
   c. $A =$ surface area
   d. $e =$ emissivity (0 to 1)
      i. ratio of total radiant energy emitted per unit time per unit area of emitting surface of a given substance at a specified wavelength and emitting temperature to the emittance of an ideal blackbody at the same specified wavelength and emitting temperature
      ii. emissivity of an ideal absorber is 1 (black body)
         (black body is also an ideal emitter)
      iii. emissivity of an white body is 0
         (white body is also an non-emitter)
      iv. emissivity is a slight function of temperature
      v. Kirchoff's law: ratio of emissivity to absorbtivity for a specified wavelength and emitting temperature is the same as that for an ideal black body at the same specified wavelength and emitting temperature.
4. Just as an object radiates energy continuously it also absorbs energy (else it would expend all of its energy and temperature would be 0K)
   a. A body absorbs energy emitted by other objects
   b. Given a body of temperature $T$, and a surrounding temperature of $T_0$, the net energy gained or lost is
      $$P_{\text{net}} = \sigma A e (T^4 - T_0^4)$$
   c. equilibrium occurs when a body emits and absorbs radiation at the same rate -- its temperature remains constant
      i. if an object is hotter than its surroundings it cools
      ii. visa-versa