Class 23 - Thermodynamics review

Thermal Equilibrium

If two objects with different temperatures are brought into contact with one another, thermal energy will flow from one to another until the temperatures are the same, and we then say that the objects are in thermal equilibrium.


“If two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.”

Thermal Expansion

Most, but not all, materials expand when heated. The change in length of material due to linear thermal expansion is

\[ \Delta l = \alpha l_0 \Delta T \]

\( \alpha \) is the coefficient of linear expansion of the material, measured in \((^\circ\text{C})^{-1}\).

The length of the object after its temperature has been changed by \( \Delta T \) is

\[ l = l_0(1 + \alpha \Delta T) \]

A material expands in all directions, and if we are interested in the volume changes of a rectangular object, that is isotropic, meaning it expands in the same way in all directions, then

\[ \Delta V = \beta V_0 \Delta T \]

\[ V_0 = l_0 w_0 h_0 \rightarrow V = l_0(1 + \alpha \Delta T)w_0(1 + \alpha \Delta T)h_0(1 + \alpha \Delta T) \]

\[ \Delta V = V - V_0 = V_0(1 + \alpha \Delta T)^3 - V_0 = V_0[3(\alpha \Delta T) + 3(\alpha \Delta T)^2 + (\alpha \Delta T)^3] \]

If \( \alpha \Delta T \ll 1 \) then \( \beta \approx 3\alpha \)

Ideal Gas Law

A mole of gas is a given number of molecules, Avagadro’s number, \( N_A = 6.02 \times 10^{23} \). If we have a certain mass \( m \) of a gas which has a certain molecular mass [http://en.wikipedia.org/wiki/Molecular_mass] (measured in atomic mass units, u, which are also the number of grams per mole.), the the number of moles \( n \) is given by

\[ n = \frac{m[\text{g}]}{\text{molecular mass}[\text{g/mol}]} \]

and

\[ PV = nRT \] where \( R = 8.314 \text{J/(mol.K)} \)
The ideal gas law can also be written in terms of the number of molecules

\[ PV = nRT = \frac{N}{N_A} RT = NkT \]

where \( k = \frac{R}{N_A} = \frac{8.314 J/(\text{mol.K})}{6.02 \times 10^{23}} = 1.38 \times 10^{-23} \text{ J/K} \) is the Boltzmann Constant [http://en.wikipedia.org/wiki/Boltzmann_constant].

### The Maxwell-Boltzmann distribution

The average kinetic energy of molecules in a monatomic ideal gas is

\[ \bar{K} = \frac{1}{2} mv^2 = \frac{3}{2} kT \]

\[ f(v) = 4\pi \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{1}{2} \frac{mv^2}{kT}} \]

### Heat transfer

**Conduction**—Primary mechanism for solids in thermal contact with each other. The heat flow \( \Delta Q \) during a time interval \( \Delta t \) in a conductor of length \( l \) and area \( A \) which connects two objects which have temperature \( T_1 \) and \( T_2 \) is

\[ \frac{\Delta Q}{\Delta t} = kA \frac{T_1 - T_2}{l} \]

which in differential form is

\[ \frac{dQ}{dt} = -kA \frac{dT}{dx} \]

**Convection**—Movements of molecules in a gas or liquid.

**Radiation**—Electromagnetic transmission of heat, does not require a medium.

\[ \frac{\Delta W}{\Delta t} = \epsilon \sigma AT^4 \]

\( \sigma = 5.67 \times 10^{-8} \text{ W/m}^2 \text{K}^4 \) and \( \epsilon \) is the emissivity of the surface, a perfect surface for emission or absorption (a black surface) has an emissivity of 1, whereas a shiny surface that neither absorbs or transmits would have an emissivity of zero. Most materials are somewhere in between these two limits.

### Specific Heat Capacity

A quantity of heat, \( Q \), flowing into an object leads to a change in the temperature of the object, \( \Delta T \), which is proportional to it's mass \( m \) and a characteristic quantity of the material, it's specific heat, \( c \)

\[ Q = mc\Delta T \]

We can see that heat flowing in to an object is positive \( \Delta T > 0 \) and heat flowing out is negative \( \Delta T < 0 \)

The specific heat is the heat capacity [http://en.wikipedia.org/wiki/Heat_capacity] per a unit of mass, in
SI the units of specific heat are $\frac{J}{kg\cdot K}$.

**Isolated Systems**

The assumption of an isolated system is very useful in problem solving as it says that the sum of the heat transfers in the system must be zero.

$$\Sigma Q = 0$$

In a system where the different objects start at different temperatures, but eventually come to an equilibrium temperature $T$,

$$\Sigma Q = m_1 c_1 (T - T_{i1}) + m_2 c_2 (T - T_{i2}) + ..$$

**Latent Heat**

Phase changes from a low temperature phases to a high temperature phase require a certain amount of heat, called the latent heat [http://en.wikipedia.org/wiki/Latent_heat].

The latent heat of fusion, $L_f$, refers to a change from solid to liquid and the latent heat of vaporization, $L_v$, refers to a change from liquid to gas. The heat required to change a mass $m$ of a substance from one phase to another is

$$Q = mL$$

During a change from one phase to another the temperature of the system remains constant.

**First Law of Thermodynamics**

The first law of thermodynamics [http://en.wikipedia.org/wiki/First_law_of_thermodynamics], dictates how internal energy, heat and work are related to each other. For a closed system the first law states that the change in the internal energy of a system, $\Delta E_{int}$, is the sum of the heat added to the system $Q$ and the net work done by the system $W$.

$$\Delta E_{int} = Q - W$$

The table shows some of the results that apply to a particular kind of thermal process

<table>
<thead>
<tr>
<th>Process</th>
<th>Constant</th>
<th>$\Delta E_{int}$</th>
<th>Q</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isothermal</td>
<td>$T$</td>
<td>0</td>
<td>$Q=W$</td>
<td>$W=Q$</td>
</tr>
<tr>
<td>Isobaric</td>
<td>$P$</td>
<td>$Q-P\Delta V$</td>
<td>$\Delta E_{int}+P\Delta V$</td>
<td>$P\Delta V$</td>
</tr>
<tr>
<td>Isovolumetric</td>
<td>$V$</td>
<td>$Q$</td>
<td>$\Delta E_{int}$</td>
<td>0</td>
</tr>
<tr>
<td>Adiabatic</td>
<td>-$W$</td>
<td>0</td>
<td></td>
<td>-$\Delta E_{int}$</td>
</tr>
</tbody>
</table>

**Path dependence of the work**

For an ideal gas $P = \frac{nRT}{V}$, so for an isothermal process

$$W = \int_{V_A}^{V_B} P \, dV = nRT \int_{V_A}^{V_B} \frac{dV}{V} = nRT \ln \frac{V_B}{V_A}$$
In an isobaric process the pressure is constant so the work is

\[ W = \int_{V_A}^{V_B} P \, dV = P(V_B - V_A) = P \Delta V \]

and if the system is an ideal gas

\[ W = P(V_B - V_A) = nRT_B(1 - \frac{V_A}{V_B}) = nRT_A\left(\frac{V_B}{V_A} - 1\right) \]

In an isovolumetric process the work done is zero

\[ W = 0 \]

**Molar Specific Heat for Gases**

For an ideal gas \( c_{P,m} - c_{V,m} = R \)

The equipartition theorem \([\text{http://en.wikipedia.org/wiki/Equipartition_theorem}]\) can be used to explain the higher heat capacity of more complicated gases. The equipartition theorem states that energy is equally shared between the different degrees of freedom the molecules in the gas have.

\[ W = \int_{V_A}^{V_B} P \, dV = P(V_B - V_A) = nRT_B(1 - \frac{V_A}{V_B}) = nRT_A\left(\frac{V_B}{V_A} - 1\right) \]

Each degree of translational or rotational freedom contributes \( \frac{1}{2} R \) to the molar specific heat at constant volume \( c_{V,m} \)

**Quasistatic adiabatic expansion of an ideal gas**

\[ PV^\gamma = \text{constant} \]

\[ \gamma = \frac{c_{P,m}}{c_{V,m}} \]
The second law of thermodynamics

Heat cannot spontaneously flow from a cold object to a hot one, whereas the reverse, a spontaneous flow of heat from a hot object to a cold one, is possible.

or

No device is possible whose sole effect is to transform a given amount of heat directly into work.

Heat Engine and Refrigerators

\[ Q_H = W + Q_L \]

Carnot Cycle

\[ e = \frac{W}{Q_H} \]

\[ e = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \]
Problem 20.10

A problem that uses the result we derived for the efficiency of the Carnot cycle as a function of $T_H$ and $T_L$. Don’t forget to pay attention to the correct units for temperature.

Problem 20.18

Another Carnot cycle problem, but this time you will have to look at the derivation rather than just the end results.

Start from conservation of energy

$W = Q_H - Q_L$

and use the equations for the two heats to arrive at an expression that links the work done to the difference in temperature.

Now you will need to find a way to change this equation so that you only have one temperature and all other terms are known.

You can find an expression that links the ratio of the temperatures $T_H$ and $T_H$ to the ratio of the volumes $V_C$ and $V_D$ by considering that

$P_B V_B = nRT_H$
$P_C V_C = nRT_L$

The last equation gives

$$e = 1 - \frac{T_L}{T_H}$$
\[ \frac{P_B V_B}{P_C V_C} = \frac{V_C^{\gamma^{-1}}}{V_B^{\gamma^{-1}}} = (\frac{V_C}{V_B})^{\gamma^{-1}} \]

which can be used with the first two to get an expression only in terms of temperatures and volumes.

**Problem 20.29**

In using the Carnot cycle as a refrigerator we cool by the removal of \( Q_L \) from the low temperature reservoir.

The first part of this question requires us to first find an amount of heat to freeze water into ice. To do this we need to use the specific heat of water (4186 J/kg/K), and ice (2100 J/kg/K) and also the latent heat of fusion for water (333 kJ/kg).

We then make use of the fact that

\[ \frac{Q_L}{Q_H} = \frac{T_L}{T_H} \quad \text{and} \quad Q_H = W + Q_L \]

The second part of the problem requires a similar approach, but less heat is required as you only freeze the water to \( 0^\circ C \). Once you have the work it's pretty easy to work out the time when you know the power.

**Otto Cycle**

\[ e = 1 - (\frac{V_A}{V_B})^{1-\gamma} \]

**Problem 20.21**

This time we are looking at the Otto cycle. You'll need to use equations that link temperature and
volume that are derived using the equations for an adiabatic process.

\[ T_A V_A^{\gamma-1} = T_B V_B^{\gamma-1} \]

\[ \frac{V_A^{\gamma-1}}{V_B^{\gamma-1}} = \frac{T_B}{T_A} \]

\[ \left( \frac{V_A}{V_B} \right)^{\gamma-1} = \frac{T_B}{T_A} \]

\[ \frac{V_A}{V_B} = \left( \frac{T_B}{T_A} \right)^{\frac{1}{\gamma-1}} \]

**Entropy**

We will define the change in entropy in a reversible process at constant temperature as

\[ \Delta S = \frac{Q}{T} \]

If we want to treat non-constant temperature cases we can express the change of entropy in differential form

\[ dS = \frac{dQ}{T} \]

and then the change in entropy in going from state \( a \) to \( b \) will be

\[ \Delta S = S_b - S_a = \int_a^b dS = \int_a^b \frac{dQ}{T} \]

As an example, if we take an object which is cooling by heat lost to the environment through a quasistatic reversible process where \( dQ = mc \, dT \)

\[ \Delta S_{\text{object}} = \int \frac{dQ}{T} = mc \int_{T_1}^{T_2} \frac{dT}{T} = mc \ln \frac{T_2}{T_1} = -mc \ln \frac{T_1}{T_2} \]

**Problem 20.39**

In this problem the gas expands isothermally, so we can use

\[ \Delta S = \frac{Q}{T} \]

Our main job is to find the heat in an isothermal expansion. This is the same as the work done by the gas in the expansion. You’ll need to use the ideal gas law to get the volume from the given pressure.

**Problem 20.46**

This is a mixing problem. The first part requires you to use specific heats of the two objects coming to equal temperature to find the final temperature.

The second part requires you to find the entropy change of the system.

Each object will have an entropy change:
\[ \Delta S_{\text{object}} = \int \frac{dQ}{T} = mc \int_{T_{\text{initial}}}^{T_{\text{final}}} \frac{dT}{T} = mc \ln \frac{T_{\text{final}}}{T_{\text{initial}}} \]

find the entropy change of each object and sum them for the total entropy.