Week 5 Key Concepts

- The **first law of thermodynamics**: $\Delta U = Q + W$ - the change in internal energy is the sum of Q, heat entering the system, and W, work done on the system. This is just energy conservation.
- A **perpetual motion machine** runs for ever without the need for fuel.
- A **function of state** is a quantity in the system that only depends on the state of the system and not on the path taken to carry out the process under study.
- A process is **reversible** if an infinitesimal change in the surroundings can reverse the direction of the process.
- The **work done on** a compressed gas is given by $W_R = -\int_{V_1}^{V_2} PdV$.
- The **heat capacity at constant pressure** $C_p = \frac{dQ}{dT}$ has two contributions $C_p = C_V + R$ - the internal energy changes measured by C_V and work is done by the gas R.
- An **isothermal expansion** occurs at constant temperature - any work done is provided from the heat bath.
- An **adiabatic expansion** occurs with no heat exchange and any work done must come from the internal energy. Here PV^γ =constant ($\gamma = C_p/C_V$).
- **Joule expansion:** A gas expands into a vacuum . It receives no heat, nor has work done on it so remains at the same temperature ($dU = 0$).

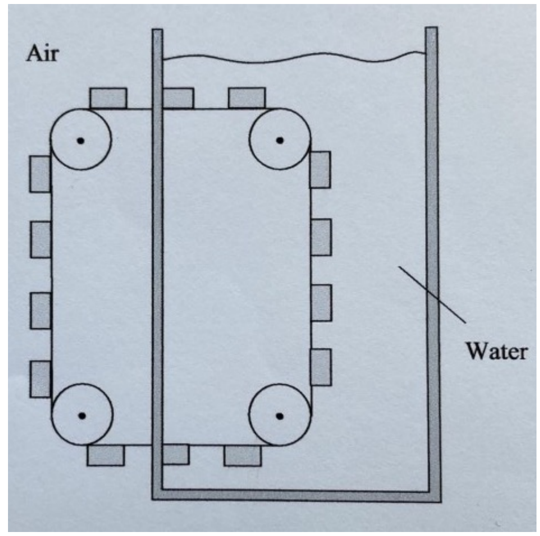
Tutorial problems

1. A hollow iron box sinking in the sea collapses catastrophically at a depth of 3600m. If the volume of the box is 0.05m^3, estimate the energy released during the collapse.
2. Explain whether the following processes are thermodynamically reversible or irreversible? You may assume as perfect conditions as help (eg no friction, infinite time etc).

   1) A saturated solution of a salt is heated, causing some of the solid salt to dissolve.
   2) a grain of salt is dissolved in a litre of water.
   3) A Joule expansion.
   4) A car tyre is inflated.
3. Consider the height of a hill $h(x, y)$. What are the meaning at a point of $\frac{\partial h}{\partial x}$and $\frac{\partial h}{\partial y}$? What property of $h(x, y)$ ensures that

$$\delta h = \frac{\partial h}{\partial x}\delta x + \frac{\partial h}{\partial y}\delta y$$

4. The figure shows a proposed perpetual motion machine. It comprises a series of boxes attached to a moveable belt. Half of the belt is immersed in water while the other half is in air. The boxes pass from water to air and then back through gates that let no water out. From Archimedes' Principle, the boxes in the water experience an upwards force compared to those in air, equal to the weight of the water they displace, and so the whole belt turns continuously counter-clockwise.
   This would violate the First law, of course, and so can't be true. Explain the error in terms of forces.



Problem Class Questions

1. A sample of ideal gas has heat capacity at constant volume $C_V = 20.8$ JK^{-1}. The gas is heated and its temperature rises by 2K. At the same time it expands, doing 16.6J of work pushing back the surroundings. What is the measured heat capacity of the gas?

2. Consider the reaction occurring when 50g of iron (of molar mass 55.85g mol^{-1}) are immersed in hydrochloric acid at a temperature of 25° C:
   $$Fe + 2HCl \rightarrow FeCl_2 + H_2$$
   Calculate the work done when the reaction takes place:
   a. in a closed vessel (constant volume)
   b. in an open beaker.

3. A mole of gas has volume 0.024 m^3 and an internal energy dependent on temperature and volume according to
   $$\left(\frac{\partial U}{\partial T}\right)_V = 25\text{J K}^{-1} \quad \text{and} \left(\frac{\partial U}{\partial V}\right)_T = 630\text{J m}^{-3}$$
   Explain why the gas is not an ideal gas.
   The gas undergoes a Joule expansion, doubling in volume. Assuming that the derivatives above remain constant, calculate the change in temperature of the gas.

4. When a rubber band under constant tension is heated, it contracts. How can this be expressed mathematically in terms of a partial derivative involving the temperature of the band T, its length L and tension F?
   Assuming the internal energy of the rubber is a function of temperature alone, and allowing for the work of stretching it but neglecting PdV work, show from the First law that the heat capacity of the rubber band under constant tension C_F is larger than the heat capacity at constant length, C_L.