Thermodynamics HW #2 Solutions

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1. Rooms A and B are *not* in thermal equilibrium since they are not at the same temperature. We expect the rooms to nevertheless be in mechanical equilibrium so that the pressure is everywhere equal. In order for this to occur regions of lower temperature should be denser so that $P = nkT$ is constant, where $n \equiv N/V$ is the density. Therefore we would expect the cold room to possess the larger air mass.

2. The adsorbate coverage can be described by the ratio $N_{\mathrm{H_2O}}/N_{\mathrm{Si}}$ where $N_{\mathrm{H_2O}}$ is the number of adsorbed water molecules and N_{Si} is the number of surface silicon atoms on the face pointing towards the hole.

   To determine N_{Si} we inspect the silicon unit cell[1] and notice each of the faces (all 8 are equivalent) contain 2 whole silicon atoms (1 in the center and 4 quarter atoms at the corners) and the area of each face is d^2, where $d = 543\mathrm{pm}$. Therefore

   $$N_{\mathrm{Si}} = 2\frac{A}{d^2}$$

   The number of adsorbed water molecules $N_{\mathrm{H_2O}}$ is given by the product $2r\Delta t$ of the rate r at which molecules leave chamber 1 and the time Δt since the surface was cleaned. The factor 2 comes from water decomposing on the silicon surface and bonding with two silicon surface atoms. The time before the surface is dirty (i.e. 10% coverage) is then given by $\Delta t = .1\frac{A/d^2}{r}$ The rate r we can determine using the microscopic model of the ideal gas (Schroeder section 1.2). Consider a patch on a wall of area a. A water molecule with a velocity component v in a direction perpendicular to the patch will collide with that patch with an average frequency of $\delta r = v\frac{a}{2V}$, where V is the volume of the container (make sure it's clear to you why). If there are N water molecules in the chamber total, then the total collision r frequency will be

   $$r = Na\frac{\bar{v}}{2V} = \frac{1}{2}a\frac{P}{kT}\bar{v}$$

   , where $\bar{v}$ is the average velocity and in the second step we use the ideal gas law. Making the approximation $\bar{v} \approx \sqrt{\bar{v^2}}$ and applying Schroeder equation 1.15 we find

   $$r = \frac{1}{2}a\frac{P}{kT}\sqrt{\frac{kT}{m}} = \frac{1}{2}a\frac{P}{\sqrt{mkT}}$$

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[1] http://hyperphysics.phy-astr.gsu.edu/hbase/Solids/sili2.html

From here we note that the above derivation for r works equally well for the describing the rate of water molecules entering a hole in the wall of area a. We find at last

$$\begin{aligned}\Delta t &= .1\frac{2A\sqrt{mkT}}{aPd^2} \\ &= .2\frac{1\text{cm}^2}{(543\text{pm})^2}\frac{\sqrt{\frac{18}{6.02\times10^{23}}4.14\times10^{-21}\text{kg}\,\text{m}\,\text{s}^{-1}}}{1\times10^{-5}\,\text{kg/s}^2\text{m}\times1\text{mm}^2} \\ &\approx 2400\text{s}\end{aligned}$$

3. Since the relation $P = IV$ for power dissipation in a resistor holds indepedently of the relative temperatures of the resistor and its power source (in this case battery), we would conclude that battery → resistor energy is flow is not heat transfer and is thus work.

   The situation is different for the resistor → water energy flow In this case we would expect to reverse the direction of energy transfer by placing the resistor in a hot water bath. This consideration leads us to conclude the energy transfer is a form of heat flow.

4. (a) The work is simply the negative of the integral under the curves. Therefore
      - A has negative work
      - B has no work
      - C has positive work

   (b) For the energy we assume that all non-frozen degrees of freedom are quadratic so that from the equipartition theorem we get

   $$U = cNkT = cPV$$

   for some positive constant c. From this we see that
      - A positive (V increases at fixed P)
      - B positive (P increases at fixed V)
      - C negative (P and V simultaneously decreasing)

   (c) From conservation of energy
      - A positive (Q must add to W which is negative to yield a positive ΔU)
      - B positive (Q must add to W which is zero to yield a positive ΔU)
      - C negative (Q must add to W which is positive to yield a negative ΔU)

   (d) The right going integral is the negative work and vice versa so the total work is positive since the left going integral is larger. Since $U \propto PV$ the final energy is equal to the initial energy. Therefore the heat flow must be negative so that when added to the work we obtain zero energy change. This process achieves transfer of heat *out* of the system via an input of work *into* it.

5. Since diesel fuel consists of molecules that are long hydrocarbon chains, we will need many more oxygen molecules than diesel fuel molecules to fully combust the fuel. Since the oxygen molecules are obtained from the air, and oxygen composes only a small ($\approx 20\%$) fraction of air, then the piston chamber will consist almost entirely of air, which in turn is composed almost entirely ($\approx 80\%$) of N_2, which has $f = 5$ degrees of freedom.

   From Schroeder equation (1.38) we then find that

   $$T_f = 20^{2/5}T_o \approx 1000^\circ K$$

   At this high a temperature the molecules have enough kinetic energy to overcome the barrier to reaction on their own and do not require an initiating spark.