Chemistry 456A (10:30AM Bagley 154)

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Problem Set 2B (due Day, 9PM Friday, 1/13/12)

Q1) We already showed that when a single weight is placed on the end of the spring the stored energy is less than the work done to stretch the spring. What is the factor between the work and energy?. Eg For a one step process, $\Delta E = \frac{1}{2} k_s \ell^2$, and the work $w = mgh$ where $h = \ell$, and the force balance requires that $mg = k\ell$. In this case then the work is twice the energy stored in the spring, $w = 2\Delta E$ (for a single step). In the next step we added a second weight and the spring was stretched an additional distance and the total energy stored in the spring is $\Delta E = 2k_s \ell^2$. The total work is the sum of the first and second steps. $w = mg\ell + 2mg\ell = 3mg\ell = 3k_s \ell^2$, the work is still larger than the energy but the fraction is less: $w = \frac{3}{2}\Delta E$ (for two steps). So the question is: If we repeat the process N times, the work applied and the internal energy will be related by $w = f\Delta E$, so what is $f = f(N)$?

Q1a) What is the total distance the spring will be stretched by adding N weights, each of mass m, onto the spring?

$$\begin{aligned} mg &= k\ell \\ Nmg &= k(N\ell) \end{aligned}$$

Q1b) Determine the amount of energy stored in the spring when N weights of mass m are loaded onto the spring.

$$\Delta E = \frac{1}{2} k (N\ell)^2$$

Q1c) What is the total work done by adding N weights, each of mass m, sequentially on the spring as the spring is stretched? Write your answer in terms of N and $k_s \ell^2$.

$$\begin{aligned} w &= mg\ell\{1+2+3+4+\cdots N\} \\ w &= mg\ell \frac{1}{2} N(N+1) = k\ell^2 \frac{1}{2} N(N+1) \end{aligned}$$

Q1d) Now find the relation $w = f\Delta E$, and f as a function of N.

$$\Delta E = N^2 \left\{ \frac{1}{2} k\ell^2 \right\}$$

$$w = \left\{ k\ell^2 \frac{1}{2} \right\} N(N+1)$$

$$\frac{\Delta E}{w} = \frac{N^2}{N(N+1)} = \frac{N}{(N+1)}$$

$$w = \frac{(N+1)}{N} \Delta E$$

Q1e) What is the heat that is generated by stretching the spring?

$$\Delta E = q + w$$

$$q = \Delta E - w = -\left\{ k\ell^2 \frac{1}{2} \right\} \left(N(N+1) - N^2 \right)$$

$$q = -N \left\{ k\ell^2 \frac{1}{2} \right\}$$

Each step produces the same amount of heat (exothermic).

Q1f) From your results, show that the work that goes into the spring equals the energy stored in the spring for a large number of weights.

At first glance it looks like the heat does not go to zero. But relative to the work or the energy change it does. If we are going a finite distance so that

$$w = \lim_{N \to \infty} \frac{(N+1)}{N} \Delta E = \Delta E$$

So the work and energy are finite despite the number of steps. The heat goes to zero as N goes to infinity and the work and heat are equal.

Q1g) We are interested in the reversible work, and the reversible work is that wherein the system can be increased infinitesimally forward or backward at every step along the way whint the addition (or removal) of an infinitesimally small amount of mass. So to do this we imagine that the individual masses are very small, $m \to dm$ and the length increase per step is also small: $\ell \to d\ell$, and the number of masses is such that the total length is $L = Nd\ell$. And the total mass is $M = Nm = Ndm$ Compare the reversible work with the internal energy stored.

$$L = N\ell = Nd\ell$$
$$\Delta E = \left\{ kL^2 \frac{1}{2} \right\}$$
$$w = \frac{(N+1)}{N}\Delta E$$
$$q = -\frac{1}{N}\left\{ kL^2 \frac{1}{2} \right\}$$

Q1h) Compute the heat that is generated for the case of reversible work.

From the above equation, we see that q goes to zero as N goes to infinity, as long as the total length remains finite.

Q1i) Compare the equation of state, EoS, for the spring with the equation of state for an ideal gas. Note similarities and differences, and comment on the role of temperature in the EoS of the spring.

$$PV = nRT$$
$$mg = k\ell$$

The two are really quite similar. Especially if you rewrite the I.G. EoS in terms of concentration C=n/V then $P = CRT$. Both equations connect the various parameters that define the physical system. The pressure in the spring is generated by the force and so the Pressure and the mass are rather similar, mg is a force and pressure is a force per unit area (along the direction of force). The length is the size of the system and so is like concentration, and the spring force constant is the one part that might depend on the Temperature, so k is analogous to the RT term for the gas. In fact for a rubber band-type spring, k is proportional to the temperature. However dependencies are quite different, for example for the I.G. the volume decreases as the external pressure goes up; for the spring the length increases as the external force goes up.

Q2a) The lead bricks we used in class to compress the gas are about 14kg each. The pistons are each about 1cm across, and there are 2 of them. How much pressure does one brick generate on one (or each) cylinder?

$$P = \frac{mg}{A} = \frac{(14 \cdot 9.8)/2}{\pi r^2} = \frac{68.6}{\pi \left(0.5 \cdot 10^{-2}\right)^2} = 870kPa$$

The lead weight almost generates one atmosphere of pressure (which is 101kPa).

So this is about 8 Atm, which is far too large from the demo in class. If on the other hand, the brick weighs 11 kg, and the piston diameter is 2.5 cm then the pressure is one atm, and that is about right.

$$P = \frac{F}{A} = \frac{mg}{\pi r^2} = \frac{11 \cdot 9.8/2}{\pi \left(2.5 \cdot 10^{-2} \big/ 2\right)^2} = 110 kPa \sim 1 Atm$$

Q2b) The piston is set to 40 mls before the lead brick is added. After the lead brick is added the piston reads about 25 mls. What pressure would produce that change? Assume the temperature of the gas remains constant in equilibrium with the room, and that the ideal gas EoS can be used. How does the pressure needed to compress the gas that far compare with the estimate of the pressure generated by the lead brick in part a?

$$\begin{aligned} P_1 V_1 &= nRT = P_2 V_2 \\ 1 \cdot 40 &= P_2 \cdot 25 \\ P_2 &= 1.6 Atm \end{aligned}$$

So the mass of the brick is overstated or the diameter of the cylinder was poorly measured, because we only need .6 Atm from the brick, but in part a) got 7 atm. If the diameter were 2.5 rather than 0.5 cm and the mass of the brick were 10kg, then the estimated pressure and the pressure inferred from the ideal gas would be in agreement.

Q2c) What is the work the brick did on the gas in part b? How much heat was transferred in this process and what direction did the heat flow. Use the relation of ΔU to temperature for the I.G.

The work the brick did was the external force through a distance. Or in terms of pressure it is Pressure (external) times volume change:

$$w = F_{ext} \cdot h = \left(\frac{F_{ext}}{Area} \cdot \right)(h \cdot Area) = -P_{Ext} \cdot \Delta V$$

$$w = -1.6 Atm \cdot (25 - 40cm) = 1.6 * 15 \cdot 10^{-3} liter - Atm$$

$$w = 1.6 * 15 \cdot 10^{-3} \cdot 101J = 2.4J$$

Q2d) Remove the brick and let the gas re-expand back to its original volume (40 mls). How much work did the gas do? Compare the amount of work the gas did under expansion to the amount of work the system did to compress the gas (part c).

The gas did less work because the external pressure is 1.0 not 1.6 so the gas work is

$$w = -1.0 * 15 \cdot 10^{-3} \cdot 101J = -1.5J$$

Q2e) Under re-expansion how much heat flows (at constant temperature) and in what direction?

The expansion work is negative and the internal energy change is zero because the temperature does not change, so the heat q=+1.5J>0 so heat must flow into the system because q is positive. $0 = \Delta E = q + w$