Chemistry C3102-2006: Polymers Section

HOMEWORK #3

The aim of this homework is to use demonstrate how one would stretch or pull a chain isothermally or adiabatically.

Due Friday, May 12

1. Using the adiabatic expansion of an ideal gas as an analogy, construct an expression for the temperature change of an rubber band (modelled as an ideal chain) as it is adiabatically stretched.

The first law of thermodynamics is

$$\Delta U = \delta q - \delta w$$

In an adiabatic process, $\delta q \to 0$, and consequently the temperature must change leading to a change in the internal energy, ΔU , of the amount $C_V dT$:

$$C_v dT = 0 - \delta w.$$

here δw is the work done by the chain, or $-\delta w$ is the work done on the chain. The work done on the chain to increase its length is -fdR, or substituting in the ideal or entropic force,

$$f = -(nN_ak_B)T\frac{3R}{Na^2} = -n\mathcal{R}T\frac{3R}{Na^2}$$

(where I have inserted Avogadro's number because C_v is in molar units, and I let n be the number of moles of chains and $\mathcal{R} = N_a k_B$):

$$C_v dT = n\mathcal{R} \frac{3R}{Na^2} dR$$

$$C_v \frac{dT}{T} = \frac{3n\mathcal{R}}{Na^2} R dR$$

$$C_v \ln\left[\frac{T_f}{T_i}\right] = \frac{3n\mathcal{R}}{2Na^2} (R_f^2 - R_i^2)$$

or

$$T_f = T_i \exp\left[\frac{3n\mathcal{R}}{2C_v N a^2} (R_f^2 - R_i^2)\right]$$

Thus, when you stretch the chain adiabatically, you are doing work on the system using an external force and this work is converted into internal energy of the system, and hence the temperature rise. This is completely opposite to what happens when you adiabatically expand an ideal gas (the temperature decreases) and the difference is that the work terms in gas expansion and in chain stretching are of opposite sign. In the first case (gas expansion) the work is done BY the system while in the second (the stretched chain) work is done ON the system.

2. Construct an expression for the temperature change of an end-tethered chain that is adiabatically squashed between two infinite plates.

The first law of thermodynamics is

$$\Delta U = \delta q - \delta w$$

In an adiabatic process, $\delta q \to 0$, and consequently the temperature must change leading to a change in the internal energy, ΔU , of the amount $C_v dT$, where we let C_v represent the heat capacity of the chain and ideal gas contained in the slit.

$$C_v dT = 0 - \delta w$$

Here there are 2 types of work being done: work to squash the chain, fdH, and work to compress the ambient gas, pdV = pAdH. To squash the chain and compress the gas, work must be done ON the system:

$$C_v dT = -f dH - pA dH$$
$$C_v dT = (-f - pA) dH$$

Now we need to insert the force/pressure laws for the ideal chain and gas. The force law for a single chain is

$$f = k_B T \frac{Na^2}{H^3},$$

However, we must convert this to molar units. Let $n_{chain} = 1/N_a$ be the number of moles of chains. Then

$$f = n_{chain} (N_a k_B) T \frac{N a^2}{H^3}$$
$$= n_{chain} \mathcal{R} T \frac{N a^2}{H^3}$$
$$f dH = n_{chain} \mathcal{R} T N a^2 \frac{dH}{H^3},$$

while the work done to compress the gas is from page 5 of the week 2 notes:

$$pdV = pAdH = \frac{n\mathcal{R}T}{AH}AdH$$
$$= n\mathcal{R}T\frac{dH}{H}$$

So then

$$C_{v}dT = (-f - pA)dH$$

$$= \mathcal{R}T\left[-n_{chain}Na^{2}\frac{dH}{H^{3}} - n\frac{dH}{H}\right]$$

$$= n\mathcal{R}T\left[-\frac{n_{chain}}{n}Na^{2}\frac{dH}{H^{3}} - n\frac{dH}{H}\right]$$

$$C_{v}\frac{dT}{T} = n\mathcal{R}\left[-\frac{n_{chain}}{n}Na^{2}\frac{dH}{H^{3}} - \frac{dH}{H}\right]$$

$$C_{v}\ln\left[\frac{T_{f}}{T_{i}}\right] = n\mathcal{R}\left[\frac{n_{chain}Na^{2}}{2n}\left(\frac{1}{H_{i}^{2}} - \frac{1}{H_{f}^{2}}\right) + \ln\left(\frac{H_{i}}{H_{f}}\right)\right]$$



Figure 1: T_f/T_i versus H_f/H_i for (a) ideal gas only (red), and (b) for ideal gas and ideal chain (green) with arbitrary $\phi = n_{chain}/nNa^2 = 0.5$. Whenever ϕ is made larger, it deviates from the ideal gas only slution more strongly. Thus, the conclusion is that the chain 'impurity' causes an increase in temperature during adiabatic compression, and most predominantly at greater compressions, $H_f/H_i \rightarrow 0$

Now from this last equation you see that for a single chain $n_{chain}/n \ll 1$, so you might be tempted to discard the contribution of the chain to the work. This is okay if the chain is small; but a *very large* single chain can make a very significant contribution as n_{chain}/nNa^2 can be of order one or larger. Note that if the chain can be ignored, $n_{chain}/nNa^2 \ll 1$, then you effectively recover the result for the expansion of the gas: as H decreases, $H_i > H_f$, the temperature increases, $T_f > T_i$.

If the chain contribution is significant, does it further increase or decrease the temperature? The easiest way to determine this is to graph it. Let $y = T_f/T_i$ and $x = H_f/H_i$ so that x goes from 1 to 0 when you squash/compress. Then, ignoring constants, but using $\phi = n_{chain}/nNa^2 < 1$ the last equation becomes roughly

$$\ln y \sim \phi(1 - \frac{1}{x^2}) + \ln\left(\frac{1}{x}\right)$$
$$y \sim \exp\left[\phi(1 - \frac{1}{x^2}) + \ln\left(\frac{1}{x}\right)\right]$$

Without the chain contribution $y_{Nochain} = \ln\left(\frac{1}{x}\right)$ (plotted in green above).