Chem 370 / ENTS 369 **Problem Set Solution** **Spring Term 2003**
Assignment 1 – The Basics **Instructor: R. Rossi**

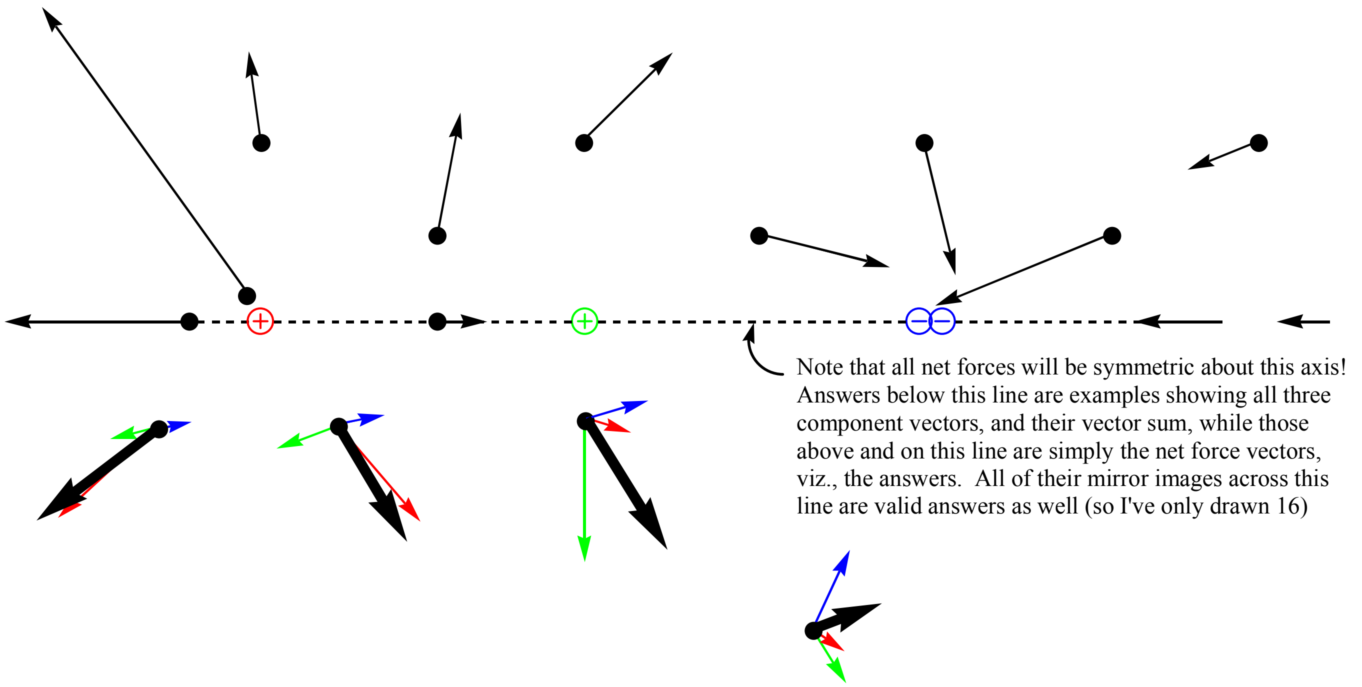
Your "official" name: Sir Gallahad, the Pure

The name you like to go by: Bill

1. I did this by estimating the force vector associated with each fixed charge, then visually calculating the net force as the vector sum of the three component forces. To get the individual force vectors right, it's important to realize the general form of the electrostatic force expression, namely,

$$F_{\text{electrostatic}} = \frac{1}{4\pi\varepsilon}\frac{q_1 q_2}{r_{12}^2}$$

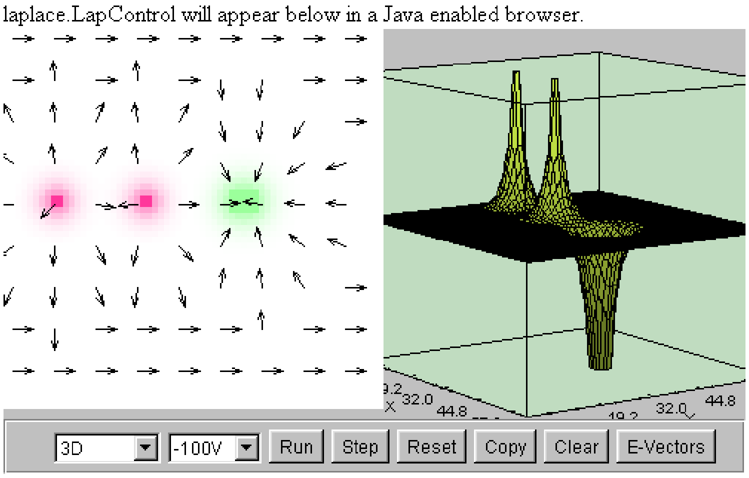
Since we are employing a positive point charge as q_1 (that's our test charge, and that it is positive effectively decides our sign convention…more on that sticky wicket as the term goes on!), the other charges will all respond to it in direct proportion to their charge (the 2– charge will have twice the attractive effect of a 1+ charge's repulsive effect at the same distance) and with an inverse square relationship to their separation from the test charge (a charge twice as far away will exert one fourth the force). My answers here are qualitative, and I expect yours to be as well, but your arrows should point in about the same directions!



Note that all net forces will be symmetric about this axis! Answers below this line are examples showing all three component vectors, and their vector sum, while those above and on this line are simply the net force vectors, viz., the answers. All of their mirror images across this line are valid answers as well (so I've only drawn 16)

Because electric field is defined as the electrostatic force per unit charge, we have effectively drawn a sampling of electric field vectors here. They tell us which way charges would like to move. A neat interactive tool to help you do something very similar with any electric potential distribution is available online at http://www.phy.davidson.edu/StuHome/anschoewe/laplace/laplace.LapControl.html. It doesn't let you pop in charges, only electric potential regions, so you can't really put in a 2– charge. The closest you can get is to put in a big ring of -100V potential, which understates the 2– charge, but it gives you the basic idea. Here's what it spits out for this situation:

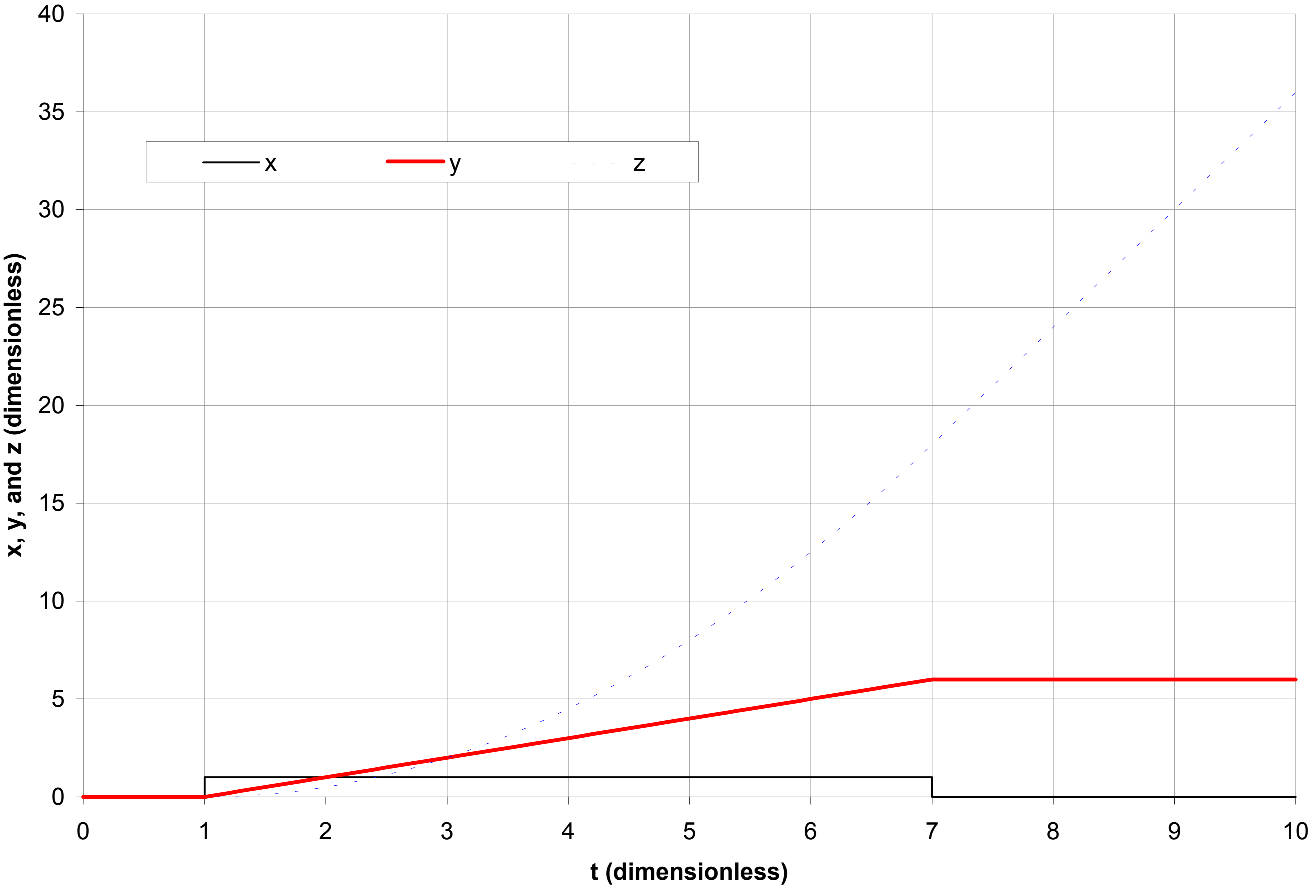
(This applet is a goodie produced by the fine folks in the Physics Department at Davidson College in North Carolina. There are fancier tools out there, too.)



laplace.LapControl will appear below in a Java enabled browser.

2. **Math** Let $\left\{ x = \begin{bmatrix} 0 \text{ for } t < 1 \\ 1 \text{ for } 1 \le t \le 7 \\ 0 \text{ for } t > 7 \end{bmatrix} \quad x = \frac{dy}{dt} \quad y = \frac{dz}{dt} \quad \text{Boundary conditions: } \begin{pmatrix} z = 0 \text{ at } t = 0 \\ y = 0 \text{ at } t = 0 \end{pmatrix} \right\}$

Sketch x, y, and z as a function of t between t = 0 and t = 10. Make your plots precise to within ±1 (vertical) unit, and draw all three on the axes below. Show your work and explain your logic on a separate paper.



Drawing out x is pretty trivial, but it lays the groundwork for the rest of the problem. Namely, we know that y starts out at zero and will remain equal to zero until x is non-zero. When x changes to one, that means that y begins increasing with a slope of one. It has a value of one at t = 2, a value of two at t = 3, and more generally y = (t-1) up until t = 7. At that point it stops increasing, because x goes back to zero. Because y = 6 at t = 7, y = 6 for all t > 7 as well. Now that we have y, it's not too hard to get z, we just have to integrate again. Because we know z starts out at zero, and that it is the integral of y, it will stay at zero until y is non-zero. Because y gradually increases from zero to one between t = 1 and t = 2, the slope of z will gradually increase from zero to one over the same region. After that, y is greater than one, and thus the slope of z should be greater than one, that is, steeper than y. The slope continues to increase with y until t = 7, when y attains a fixed value of 6, and thus z adopts and subsequently maintains a slope of +6. Note that because y is continuous around t = 7, the slope of z is also continuous there. To get the value of z at t = 7, the easiest thing to do is to calculate the area of the triangle formed by y, ½ b·h = ½ 6·6 = 18. About the only spot worth writing an equation for is z in [1,7], but here are all of them, in case you're wondering:

$$y = \begin{Bmatrix} 0 \text{ for } t < 1 \\ t\text{-}1 \text{ for } t\ [1,7] \\ 6 \text{ for } t > 7 \end{Bmatrix} \qquad z = \begin{Bmatrix} 0 \text{ for } t < 1 \\ \tfrac{1}{2}(t\text{-}1)^2 \text{ for } t\ [1,7] \\ 18+6(t\text{-}7) \text{ for } t > 7 \end{Bmatrix}$$

Note that x & y cross at (1,2), while y & z cross at (2,3)

$$y = (t-1) = \frac{dz}{dt} \text{ in } [1,7] \quad \Rightarrow \quad \int_{t=1}^{t} dz = \int_{t=1}^{t} (t-1)dt \quad \Rightarrow \quad z(t) - z(1) = \tfrac{1}{2}(t-1)^2 - \tfrac{1}{2}(1-1)^2 \quad \Rightarrow \quad z - 0 = \tfrac{1}{2}(t-1)^2 - 0$$

(This integration is done with the u-substitution u = (t-1), du = dt.)

3. There are a plethora of ways to solve this problem, but I will outline the two most "obvious" ones here. One is more microscopic, the other more macroscopic; the latter is easier, but makes it easy for you to gloss over a key insight into what's going on. Let's start with the more microscopic approach, which involves consideration of the case of a single Na atom and a single Cl atom, both in the gas phase. The energy required to pull an eletron off of our Na atom and out "to vacuum" or "to the vacuum level" (technically, that would be infinitely far away) is the first ionization energy of sodium, $IE_1[Na]$. The energy released when we let go of an electron from the vacuum level (again, technically, that means infinitely far away) and allow it to freely approach our Cl atom is the first electron affinity of chlorine, $EA_1[Cl]$. We can look up both of these values in lots of places, you will most likely turn to the CRC Handbook. I chose instead Appendix 1 of Atkins' *Inorganic Chemistry*, 2nd Ed., because as you will learn, I have a thing for electron volts, and I want you to get comfy with them too. (They are just a very small energy unit handy for talking about electron energies.) Atkins says that $IE_1[Na] = 5.138$ eV, while $EA_1[Cl] = 3.617$ eV. This means that pulling an electron off of an isolated Na atom and plopping it onto an isolated Cl atom requires a net input of $$\Delta E = +IE_1[Na] - EA_1[Cl] = 5.138\,eV - 3.617\,eV = 1.521\,eV$$
Note that this is not thermodynamically favorable! Since we are only talking about two entities, there's no entropy consideration, and the enthalpy (chemical potential energy) change for the electron transfer is positive, meaning that it is thermodynamically uphill. What's up with that?!? How can this process take place spontaneously?!? The trick is that we can get an appreciable amount of energy back by allowing the two isolated ions (Na^+ and Cl^-) generated in this process to approach each other. Being oppositely charged (+e for Na^+ and –e for Cl^-) and in the gas phase, they experience an electrostatic attractive force given by
$$F_{electrostatic} = \frac{1}{4\pi\varepsilon}\frac{q_1 q_2}{r_{12}^2} \quad \text{where } q_1 = +e,\ q_2 = -e,\ \varepsilon = \varepsilon_o, \text{ and } r_{12} = \text{the seperation between the ions}$$
The energy released by allowing them to fall together is equal to the amount of work you could extract from them doing so. Work can be obtained from a force acting over a distance, so $dW = Fdx = Fd(r_{12})$ [if we choose one of the ions as our frame of reference, then x = separation between the ions = r_{12}]. Integrating to get the total work, and thus the change in potential energy associated with the two ions coming to within distance r of each other, starting at infinite separation (that is, isolated from each other), we get:
$$\Delta PE_{electrostatic} = \int_{initial}^{final} dW = \int_{i}^{f} F_{electrostatic}dx = \int_{r_{12}=\infty}^{r_{12}=r} \frac{1}{4\pi\varepsilon}\frac{q_1 q_2}{r_{12}} dr_{12} = \frac{q_1 q_2}{4\pi\varepsilon_o}\int_{\infty}^{r}(r_{12})^{-2}\,dr_{12}$$
$$= \frac{(+e)(-e)}{4\pi\varepsilon_o}\Big[(-1)(r_{12})^{-1}\Big]_{\infty}^{r} = \frac{-e\left(1.602\times10^{-19}C\right)}{4\pi\left(8.854\times10^{-12}\,\frac{C}{V\cdot m}\right)}\left[\frac{-1}{\infty}-\frac{-1}{r}\right] = -1.440\times10^{-9}\left(\frac{1}{r}\right)eV\cdot m$$
We can now determine what value of r allows us to just break even on energy:
$$\Delta E + \Delta PE_{elect} = 0 \quad \Rightarrow \quad 1.521\,eV = 1.440\times10^{-9}\left(\frac{1}{r}\right)eV\cdot m \quad \Rightarrow \quad r = 9.467\times10^{-10}\,m$$
Golly, that seems awfully small, but you have to remember we are talking about ions here, and that this is 9.467 Å, a veritable city block in atomic terms. Atkins says that Na^+ has an ionic radius of about 1 Å, while Cl^-'s ionic radius is about 1.7 Å, so the two ions will probably snuggle up to r = (1 Å + 1.7 Å =) about 2.7 Å, much closer than the minimum needed to make the net electron-transfer + ion-approach process energetically favorable overall. Note that we have used Hess' Law here – the process we used to calculate the thermodynamics is *not* the process by which the e^- transfer might actually spontaneously occur. (The process we did the calculation for would have a 1.5 eV activation energy, which is astronomically big in atomic terms! For you chemists, it's a whopping 144 kJ/mol!) But energies are state functions, so we know that the energy change for the actual neutral-atoms-approach-and-transfer-an-electron process will be identical to that calculated here: it is path-independent. I've assumed the initial situation here to be two, and only two isolated gas phase atoms, and the final situation a gas-phase Na^+Cl^- ion pair.

The other solution I'll present to this problem is based on statistical mechanics and bulk thermodynamics. We know that we can determine the spontaneity of any chemical reaction based on the (Gibbs) free energy, which takes both enthalpic and entropic factors into properly weighted consideration. We are interested in whether the following reaction is spontaneous: $Na_{(g)} + Cl_{(g)} \rightarrow NaCl_{(g)}$ [or perhaps $NaCl_{(s)}$]
But the value of ΔG will depend on the specific conditions under which this transformation takes place, which is the tricky part of doing it this way. I have to specify, by assumption, quite a few things in order to come up with a numerical value for this reaction's ΔG. I'll pick reasonable assumptions that simplify the math as much as possible. $Na_{(s)}$ and $Cl_{2(g)}$ might seem like more reasonable phases to assume, but the problem stipulates that we have gas phase atoms, not molecules or clusters. Even so, I don't have to hypothesize a high temperature, because at any temperature Na has some vapor pressure, and in a room-temperature vacuum chamber one can easily have almost all the Na in there present as $Na_{(g)}$ (the rest being gas-phase clusters). Keeping $Cl_{(g)}$ from turning into Cl_2 is trickier, but there too, we need not go to a high temperature. (We could, up to a point; but I'm confident the reaction above stops being spontaneous at high enough temperatures!) I'd like to calculate and use $\Delta G^o(298\text{ K})$, so I will assume the following:

- All of the species involved have unit activities (that's what the ° symbol means), which means the gases have partial pressures of 1 bar (about 1 atm) and if we go with $NaCl_{(s)}$, just that there is some.
- The temperature is 298 K.
- My NaCl is present as gas-phase ion pairs, $NaCl_{(g)}$, rather than as $NaCl_{(s)}$. My rationale here is that $NaCl_{(s)}$ is definitely going to be the lower free energy state at 298 K, so if the reaction is spontaneous to form $NaCl_{(g)}$, it will definitely be spontaenous to form $NaCl_{(s)}$.

This means that some NaCl is already present when I consider this situation. If there were absolutely none present, then ΔG would be $-\infty$ (and the analysis would be meaningless, because the same is true for *any* reaction in which the activity of one of the products is nil!)!!! I have to assume some is present from the get-go in order to get any kind of reasonable statistical mechanics result. Okay, so how do I get $\Delta G^o(298\text{K})$ for this reaction. You might use the CRC, it has data for weird phases like this, but I've gone electronic. I like to use the NIST WebBook to pull up data like this…after all, it's my tax dollars at work! From http://webbook.nist.gov, I find:

$$\Delta H_f^o(298\text{K})\left[Na_{(g)}\right] = +107._{30}\ {}^{\text{kJ}}\!/\!_{\text{mol}} \qquad S^\circ(298\text{K})\left[Na_{(g)}\right] = 153.65\ \tfrac{\text{J}}{\text{mol}\cdot\text{K}}$$

$$\Delta H_f^o(298\text{K})\left[Cl_{(g)}\right] = +121.30\ {}^{\text{kJ}}\!/\!_{\text{mol}} \qquad S^\circ(298\text{K})\left[Cl_{(g)}\right] = 165.19\ \tfrac{\text{J}}{\text{mol}\cdot\text{K}}$$

$$\Delta H_f^o(298\text{K})\left[NaCl_{(g)}\right] = -181.42\ {}^{\text{kJ}}\!/\!_{\text{mol}} \qquad S^\circ(298\text{K})\left[NaCl_{(g)}\right] = 229.79\ \tfrac{\text{J}}{\text{mol}\cdot\text{K}}$$

Consequently, we apply a general equation applicable to state functions to get

$$\Delta H^o_{\text{rxn}} = \sum_i \chi_i \Delta H_f^o[i] = \left(-1\cdot\Delta H_f^o[Na_{(g)}]\right) + \left(-1\cdot\Delta H_f^o[Cl_{(g)}]\right) + \left(+1\cdot\Delta H_f^o[NaCl_{(g)}]\right)$$

$$= \left(-1\left[+107._{30}\ {}^{\text{kJ}}\!/\!_{\text{mol}}\right]\right) + \left(-1\left[+121.30\ {}^{\text{kJ}}\!/\!_{\text{mol}}\right]\right) + \left(+1\cdot\left[-181.42\ {}^{\text{kJ}}\!/\!_{\text{mol}}\right]\right) = -410._{02}\ {}^{\text{kJ}}\!/\!_{\text{mol}}$$

$$\Delta S^o_{\text{rxn}} = \sum_i \chi_i S^\circ[i] = \left(-1\cdot S^\circ[Na_{(g)}]\right) + \left(-1\cdot S^\circ[Cl_{(g)}]\right) + \left(+1\cdot S^\circ[NaCl_{(g)}]\right)$$

$$= \left(-1\left[153.65\tfrac{\text{J}}{\text{mol}\cdot\text{K}}\right]\right) + \left(-1\left[165.19\tfrac{\text{J}}{\text{mol}\cdot\text{K}}\right]\right) + \left(+1\cdot\left[229.79\tfrac{\text{J}}{\text{mol}\cdot\text{K}}\right]\right) = -89.05\tfrac{\text{J}}{\text{mol}\cdot\text{K}}$$

We can then determine ΔG^o from ΔH and ΔS, because $G \equiv H - TS$ and at fixed T, $\Delta G = \Delta H - T\Delta S$:

$$\Delta G^o_{\text{rxn}} = \Delta H^o_{\text{rxn}} - T\Delta S^o_{\text{rxn}} = -410._{02}\ {}^{\text{kJ}}\!/\!_{\text{mol}}\left(\tfrac{1000\text{ J}}{1\text{ kJ}}\right) - 298\text{ K}\left(-89.05\tfrac{\text{J}}{\text{mol}\cdot\text{K}}\right) = -410_{020}\ \tfrac{\text{J}}{\text{mol}} + 265_{37}\ \tfrac{\text{J}}{\text{mol}} = -383_{483}\ \tfrac{\text{J}}{\text{mol}}$$

Since this is clearly negative, the reaction above is spontaneous when the assumptions above hold, and by extension also when the product of the reaction is $NaCl_{(s)}$. Note that enthalpy strongly favors this reaction, while enthalpy weakly disfavors it, so at very high temperatures, where entropy decides things, relatively little NaCl would be present at equilibrium. (ΔG^o becomes zero at 4600 K, which is hot but not outlandishly hot: plasma temperatures readily exceed this, for example, so this may not be a common reaction on the sun!)