The Thermodynamics of the Dissolution of Urea

Background

We know that chemical reactions proceed with the evolution or absorption of heat. This heat flow represents differences in chemical energy associated with the rearrangement of atoms in molecules, the making and breaking of bonds to form new substances. When measured at constant pressure this is the *enthalpy change* (ΔH) for the reaction.

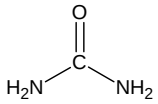
Physical changes can also involve heat. Typically the dissolving of a solid in water will involve measurable heat. There is not absolute agreement on whether dissolving itself should be categorized as wholly physical, partly chemical, etc., but intermolecular forces are certainly involved (at the very least). Regardless of the appropriate "label" for dissolving as a process there *is* an overall energy term. It is known as the **heat of solution**, ΔH_{soln}.

It may not be possible to know the precise mechanism for a particular dissolution, but in a hypothetical generalized scenario there would be at least three energy changes involved:

1. solute particles are separated from the solid mass (energy is *absorbed*, ΔH_1)
2. solvent particles move apart to make space for dissolved solute (energy is *absorbe*d, ΔH_2)
3. solute and solvent particles are attracted to one another (energy is *released*, ΔH_3)

For most solids dissolving in water, the sum of the first two terms is greater than the third and thus dissolving is frequently endothermic (ΔH_{soln} = +) and solubility *generally* increases with increasing temperature. When heats of solution become <u>very</u> highly positive it is often because the solute and solvent are dissimilar and, in the extreme case, immiscible. The old rule of "like dissolves like" is an approximation, but a good one.

The urea-water system involved in this experiment is an interesting one because it involves a sequence of enthalpy and entropy trade-offs due to the presence of strong intermolecular forces: hydrogen bonding. Urea, an amide, has the following structure:

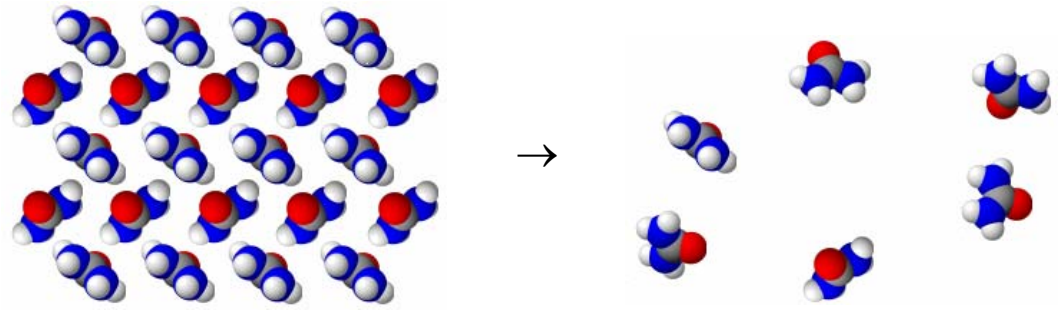


[Historically urea is a compound of some importance. In the early days of what became organic chemistry there were many who believed that organic compounds could not be synthesized in the laboratory from inorganic ingredients. Organic compounds were thought to contain a "vital force" (decidedly non-chemical) but in 1828, Friedrich Wöhler (then 28 years old) accidentally prepared urea by heating ammonium cyanate (an inorganic compound). This event opened the door to the development of modern synthetic organic chemistry.]

Because of the electronegativity of the nitrogen atom, hydrogen bonding is possible at both N-H sites in the urea molecule. There is also respectable polarity at the C=O bond and additional interactions can occur there. Urea is therefore a polar molecular solid. Its melting point is 133^{o}C.

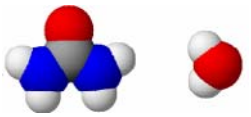
Adapted from <u>The Entropy of Dissolution of Urea</u>, Miles Pickering, J. Chem . Ed., 1987, vol. 64, p. 723

The melting point of urea suggests that fairly strong forces bind the molecules together in the solid. These forces must be overcome if the solid mass is to separate during dissolving:



Clearly this part of the dissolution process should be endothermic (i.e., $\Delta H_1 = +$)

The second step in the dissolving "process" is the disruption of the semi-structure in the solvent to make space for the solute molecules to disperse and enable the formation of a mixture. Urea molecules are not the same size as water molecules as the scale diagrams below show.



In the jostling of water molecules that would occur normally at room temperature hydrogen bonds are breaking and forming constantly and molecular clusters of various sizes come and go. But the insertion of urea molecules into this mix requires more space between the water molecules and that means added potential energy. This part of the dissolution process is therefore also endothermic ($\Delta H_2 = +$).

The final step in the rather artificial solution formation process described earlier is the interaction between solute and solvent which results in the actual solution forming. In the case of urea and water the situation looks very promising. Both substances are polar, both can hydrogen bond, and while urea is somewhat larger than water it is not grossly out of scale. We might expect fairly strong interactions between the molecules and that means ΔH_3 should be negative.

The hard part, of course, is to guess the relative magnitudes of these steps, i.e., whether the overall process will be endothermic or exothermic. If we "guess" that the breaking of hydrogen bonds in solid urea is roughly equivalent to the making of hydrogen bonds in the urea-water solution then the second step (which is somewhat endothermic) might determine the overall heat of solution. Experimentally, this is easy to settle by a simple calorimetry experiment.

Urea is quite soluble in water (1 g in 1 mL) so there is no question as to the spontaneity of the process at room temperature. This tells us something else about the dissolving of urea in water: the entropy change in the *universe* is positive.

When solids dissolve in liquids the entropy of the *system* nearly always increases. This is owing mainly to the increased freedom of movement of the solute particles as the forces which hold the solid together are overcome. When the urea molecules are trapped in the solid lattice they can only vibrate in place and these vibrational motions are limited by near neighbors. In addition, vibrational energy states are fairly far apart so the options are few at room temperature. Dispersed in the solvent, the molecules can translate and rotate as well as vibrate. The energy states for the many possible translational and rotational motions are more closely spaced than those for the vibrational states. Therefore with increased movement comes the possibility of more of those motions such as make IR spectra so complex and which aid in the dispersal of energy. Dispersal of energy is what entropy is all about.

So the entropy change for the first step in our dissolving "process" is positive (ΔS_1 = +). Also occurring in the system, the solvent molecules must move about to make space for the solute. In general this results in disruptions of the solvent-solvent forces and more freedom of movement for the solvent molecules, hence additional pathways for energy dispersal. So ΔS_2 is typically positive.

In the final step solvent and solute interactions decrease the free movement of both species to some extent and the entropy may decrease. This leaves two unknowns: what are the relative magnitudes of these three steps which occur in the *system* AND what about ΔS_{surr}?

The question about ΔS_{surr} takes us back to the question about the overall ΔH_{soln} (actually ΔH_{sys}) since the flow of heat between the system and the surroundings will determine ΔS_{surr}. If heat moves into the surroundings then the entropy there will rise. If the heat flow is in the other direction then ΔS_{surr} will be negative. Urea certainly dissolves and therefore:

$$\Delta S_{sys} + \Delta S_{surr} > 0$$

But if the solvent-solute interactions are strong enough, ΔH_{sys} (i.e., ΔH_{soln}) might be negative. This would make ΔS_{surr} positive but would also tend to make ΔS_3 more negative. If, on the other hand, ΔH_{sys} were positive, then ΔS_{surr} would be negative and so $\Delta S_1 + \Delta S_2 > |\Delta S_3 + \Delta S_{surr}|$.

As already mentioned, it is possible to find the heat of solution in the lab but determining the entropy of solution (ΔS_{soln}) is a more complicated matter. This is true for most entropy determinations, which are typically indirect. In this experiment the thermodynamic requirements for the equilibrium condition can be exploited to determine ΔS_{soln} from the readily found heat of solution and the free energy change.

In a saturated solution of urea the following equilibrium exists:

$$\text{urea}_{(s)} \leftrightarrows \text{urea}_{(aq)}$$

The equilibrium constant expression for this reaction is:

$$K_c = \frac{[\text{urea}_{(aq)}]}{[\text{urea}_{(s)}]}$$

Because the solid has *unit activity* (and a constant concentration) it is generally not given as part of the constant so this expression may be written simply as:

$$K_c = [urea_{(aq)}]$$

We know that the relationship between the equilibrium constant and the standard free energy change is:

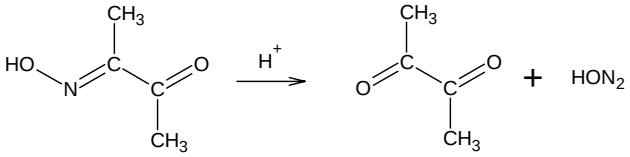
$$\Delta G^o = -RT \ln K_c$$

where **R** = 8.31 J/mol·K and **T** is in kelvins. If the concentration of urea in a saturated solution can be determined then K_c is known and it is possible to calculate the free energy change for the dissolving of urea (or at least an approximation of ΔG^o). Combined with the heat of solution from a calorimetry experiment this allows the calculation of ΔS_{soln} since:

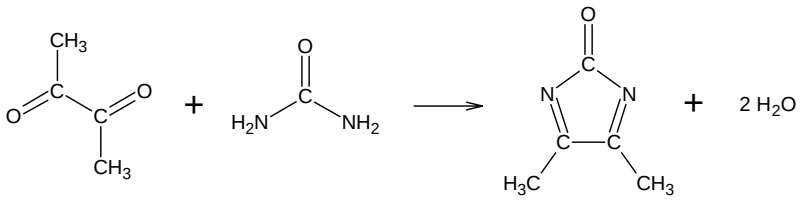
$$\Delta G_{soln} = \Delta H_{soln} - T\Delta S_{soln}$$

The measurement of urea concentration can be done by a variety of methods. In this experiment we will use an adaptation of a colorimetric method employed in clinical medicine for determining "blood urea nitrogen" (BUN). This assay is so sensitive that the saturated urea solution has to be diluted 20,000-fold to give a suitable concentration.

The diluted urea solution is combined with a test reagent which consists of an acidic solution of diacetyl monoxime and some additional minor constituents. In acidic solution the monoxime hydrolyzes to give 2,3-butanedione (which is otherwise unstable):



Upon warming, a condensation reaction occurs with the urea in the solution:



The resulting five-membered ring compound is pink. One of the other minor constituents in the test reagent intensifies the color in some unspecified way. The intensity of the color is proportional to the concentration of urea so that a comparison can be made with standards in accordance with Beer's Law.

The Experiment

There are three parts to this experiment:

- determination of the heat of solution for urea in water
- determination of the specific heat of the urea solution
- determination of the urea concentration in a saturated solution

The following non-locker materials will be provided:

- solid urea
- expanded polystyrene calorimeter
- CBL w/thermometer probes
- matched pair of resistance-heater calorimeters w/power supply and cable
- saturated urea solution [**record temperature from label**]
- 100 mL volumetric flasks
- micropipettor w/tips
- 4 urea solution standards [**record concentrations from labels**]
- six 13 x 100 mm test tubes in rack
- Fisher Model 415 Spectrophotometer w/cuvettes
- BUN reagent

The Chemicals

Urea consists of white, tetragonal prisms. On storage it may develop the odor of ammonia. It is very soluble in water, somewhat less in alcohols and glycerol. Water solutions decompose on heating. It is used in fertilizers and animal feeds. In combination with aldehydes it can be made into plastics and resins and is used extensively in the paper industry to soften cellulose fibers. It is also used to brown baked goods such as pretzels.

Diacetyl monoxime is related to dimethylglyoxime (or diacetyl dioxime) practically insoluble in water, but soluble in alcohol and ether. It hydrolyzes in acid solution to form 2,3-butanedione, a diketone. [see below]

2,3-butanedione (or diacetyl) is found in bay and other oils as well as in butter. In pure form it is a yellowish-green liquid with a quinine odor. It is soluble in about 4 parts water. It is used as a carrier of aroma of butter, vinegar, coffee and other foods.

Technique Discussion

Be sure to bring your TI-83/P calculator to lab and have the HCHEM.83G programs in memory.

The first two parts of the experiment involve a series of calorimetry measurements. The procedure for the calorimetry is typical. About 4 g of urea in 50 mL of water should give a reasonable temperature change. Although urea is quite soluble in these proportions it is wise to use a magnetic stirrer to agitate the mixture so that the dissolution occurs quickly, limiting possible heat exchange with the surroundings. The determination should be done in triplicate with the first trial reserved for the next step. Masses for the solution components are required. Although not absolutely necessary for the heat of solution determination, mixtures with very similar proportions provide a more constant specific heat.

To accurately calculate the heat involved in the temperature change of the urea solution it is necessary to know the specific heat of the mixture. Typically the addition of solute lowers the specific heat of water. One way to determine the specific heat of the mixture is to place a sample in an electrically heated calorimeter which is connected in series with an identical calorimeter containing water. As electricity flows through the circuit both solutions receive the same amount of heat energy but their temperature changes will be different owing to their different specific heats. The only unknown in this situation is the specific heat of the urea solution.

Using the first solution from the three trials allows time for the mixture to come back to room temperature. This is not absolutely necessary but it tends to give better results since heat exchange with the surroundings is less likely early in the process. The mass of the solution added to the calorimeter and the mass of water in the other calorimeter (about 50 mL) should be recorded. Filling the calorimeters before wiring them together helps to stabilize them (in any case the electricity should not be allowed to flow if the calorimeters are empty; the heaters will burn up). With the power supply set on 12 v the liquids should be heated until the water temperature has changed by about 10 degrees. Initial and final temperatures should be recorded.

[The following procedure will be done by the instructor and temperature data will be given along with the prepared solution:

About 35 g of urea should be mixed with 25 mL of 0.1% benzoic acid water solution (the benzoic acid acts as a preservative to retard bacterial growth). After vigorous stirring, the mixture is allowed to stand *at least* overnight. After recording the temperature of the solution, the mixture is then gravity filtered.]

The saturated solution must be diluted 1:20,000 using special glassware. The dilution of 1:20,000 can be made in the following fashion: remove 1000 μL (1 mL) of the saturated urea with the micropipet and place it in a clean, dry 100 mL *volumetric* flask.

The volumetric flask has a line etched on the neck somewhere. This mark was placed individually at the factory. You need to fill the flask with distilled water so that the meniscus sits on this line (at eye-level). It is *very* easy to fill over the mark because the neck of the flask is quite narrow. To avoid this common error, fill the last little bit with an eyedropper. Stopper firmly and invert *at least 20 times* to insure complete mixing. **Thorough mixing of dilutions is absolutely critical to the success of this experiment!!!!!!!!!**

Using a clean tip, 500 μL of the new solution is withdrawn and transferred to another 100 mL volumetric flask and diluted as before.

The two BUN reagents must be mixed the same day you will make the absorption measurements. To avoid wasting the solutions, the instructor will prepare this mixture in a single batch. It will be dispensed from burets.

2.5 mL of the BUN solution mixture is dispensed into each of six clean, dry test tubes. The "blank" has 0.150 mL (150 μL) of water added. The remaining five samples have an identical amount of the four standards and the diluted urea solution added. Because the test is extremely sensitive is it imperative that separate tips be used for each new solution [tips for the standards may be shared]. The six tubes should then be immersed in already *boiling* water for exactly 10 minutes, and then cooled for 5 minutes in cold tap water. Transfer the "blank" mixture to the cuvette provided. Use this solution to zero the spectrophotometer. Empty this solution back into its original test tube and rinse the cuvette with a *little* of the solution from the next tube (begin with the *lightest* solution). Discard the rinse and then fill the cuvette and measure its Absorbance at 520 nm. Continue in this way to record the Absorbance of each sample.

The Report

Your initial calculations should include:

[**you may assume the various calorimeter constants all = 0**]

1. The specific heat of the urea solution

2. The heat absorbed or released per mole of urea (i.e., ΔH_{soln})
   [best value/standard deviation, 95% confidence, relative error]

3. A calibration graph for urea at 520 nm with the BUN reagents, Absorbance vs. concentration (blank = zero concentration)

4. The concentration (M) of the diluted saturated solution (as read from the calibration graph)

5. The concentration (M) of the original saturated solution of urea

6. The free energy change, ΔG, for the dissolution of urea [relative error]

7. The entropy change, ΔS, for the dissolution of urea at the appropriate temperature [relative error]

Your conclusion to this experiment should include a brief discussion of discrepant data. The following values for the thermodynamics of the dissolution of urea are taken from *Basic Tables in Chemistry* by R. Keller:

ΔG = -6.86 kJ/mol
ΔH = +13.8 kJ/mol
ΔS = +69.4 J/mol K

A brief summary of the probable signs and magnitudes of the enthalpy and entropy changes in the hypothetical steps for the formation of the solution as described in the Background section should also be included.