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Activity-Based Approach For Teaching Aqueous Solubility, Energy, and Entropy

Laura Eisen,[†] Nadia Marano,^{*,‡} and Samantha Glazier[‡]

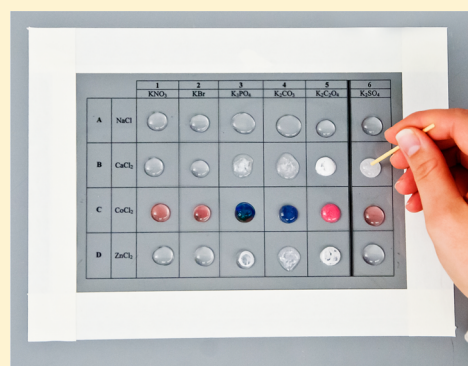
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S Supporting Information

ABSTRACT: We describe an activity-based approach for teaching aqueous solubility to introductory chemistry students that provides a more balanced presentation of the roles of energy and entropy in dissolution than is found in most general chemistry textbooks. In the first few activities, students observe that polar substances dissolve in water, whereas nonpolar substances do not, and that in some cases, dissolution is endothermic. Because energy minimization alone cannot explain these observations, we introduce entropy descriptively as another factor promoting dissolution. The increase in entropy due to mixing can counteract unfavorable energy changes, whereas unfavorable entropy changes due to reorganization of the water explain why nonpolar substances do not dissolve. In another activity, students mix combinations of positive and negative ions and formulate a simple rule that predicts the solubility of most ionic compounds: *salts in which the cations and anions are multiply charged are likely to be insoluble; other salts are likely to be soluble*. Students later discover that the sign and magnitude of the entropy changes explain why the rule works so often. Salts that are exceptions to the rule generally have unusually large enthalpies of dissolution.

KEYWORDS: First-Year Undergraduate/General, Curriculum, Hands-On Learning/Manipulatives, Inquiry-Based/Discovery Learning, Misconceptions/Discrepant Events, Hydrogen bonding, Ionic bonding, Solutions/Solvents, Thermodynamics, Water/Water Chemistry



Life exists on our planet because of liquid water, so the study of aqueous solutions is an important topic in general chemistry even though the molecular interactions are complex. Both energy minimization and entropy maximization of the system promote the total overall entropy increase that must accompany all observable processes, including dissolution. Perhaps because of the difficulty of teaching entropy or a wish to keep things simple, the importance of energy interactions tends to be overemphasized in general chemistry, and the role of entropy in dissolution is often deferred until later. We believe that it is important for general chemistry students to appreciate the role of entropy even if they cannot fully understand all aspects of the topic. There is evidence that learners understand concepts better if they are presented early and in multiple contexts, so that students who are exposed to the role of entropy in an introductory course should be better able to understand the complexities of dissolution later on.¹

In this paper, we first summarize how aqueous solubility is typically presented in general chemistry textbooks and discuss some concerns we have with the traditional presentation. Then we describe a new approach used in our classes to help our students understand key concepts of dissolution. Finally, we discuss why we believe this approach is an improvement.

■ HOW SOLUBILITY IS TYPICALLY PRESENTED IN GENERAL CHEMISTRY

Aqueous solubility is traditionally explained in terms of attractive interactions between the negative and positive regions of the water molecules and the opposing charges of the solute. The energy released as a result of these interactions is assumed to compensate for the energy required to separate the individual solute and solvent particles. Students learn the useful generalization that “like dissolves like”: that is, polar and ionic substances tend to dissolve in water, whereas nonpolar substances do not. The failure of nonpolar substances to dissolve in water is generally attributed to weak interactions between the nonpolar solute and the polar solvent.^{2–6} Because many ionic compounds are not soluble in water, students also learn a set of solubility rules that enable them to predict which ionic compounds will dissolve.^{3,5,7} In the second semester, solubility is quantitatively treated with equilibrium calculations involving K_{sp} . Solubility is presented in this manner in virtually every textbook we have encountered.

Why the Traditional Approach Can Be Improved

We believe that it is possible to teach about the cooperative contributions of energy and entropy in solubility while retaining the traditional content. When the process of dissolution is

described in terms of attractive interactions between solute and solvent, it implies that differences in solubility depend primarily on enthalpy considerations. For example, one might expect that nonpolar substances do not dissolve in water because the forces of attraction between these solutes and water are too weak to make up for the energy required to separate solute molecules and break hydrogen bonds between hydrating water molecules. If this were true, the net energy for dissolving nonpolar substances would be unfavorable. However, it has been known since the middle of the last century that this is not correct.⁸ In his seminal paper on protein denaturation, Kauzmann summarizes data from several sources to show that the enthalpy change, ΔH , for the transfer of hydrocarbons from a nonpolar solvent to water (or transfer of a pure liquid hydrocarbon to water) is negative for small aliphatic compounds and near zero for aromatic compounds.⁹ These observations are inconsistent with an enthalpy-based explanation of “like dissolves like”. Kauzmann points out that the entropy change, ΔS , is actually negative in all of these cases, which is the reason why hydrocarbons are insoluble in water.

As early as 1945, Frank and Evans recognized the role of entropy in solubility.¹⁰ They hypothesized that water forms an ordered “iceberg-like” structure around nonpolar molecules, resulting in an unfavorable entropy effect. The fact that nonpolar substances do not dissolve to any great extent in water can be explained by this unfavorable entropy change. Although several textbooks do discuss the role of entropy^{11–14} in solubility in the chapters on thermodynamics, this is most often used to explain why things are soluble rather than insoluble.^{5,15} Only rarely is entropy used qualitatively or is a discussion of the entropy of water included.^{7,16,17}

When ionic solubility is presented as a list of rules, it is difficult for students to connect solubility behavior to molecular structure. Blake has suggested a more conceptual approach when he proposes a simple solubility rule based on molecular structure: “Any salt involving a +1 cation or a –1 anion is likely to be soluble.”¹⁸ Blake’s explanation that “the attraction of oppositely charged ions is proportional to the magnitude of the charges of those ions” is characteristic of many texts.^{2,15,19,20} The implication is that salts with multiply charged ions have large lattice energies, making it difficult for them to dissociate and, therefore, decreasing their solubility. Although this is certainly true, the magnitudes of the hydration energies are also larger. Hydration energies for many salts with multiply charged ions are large enough that the net enthalpy change for dissolving the salt is negative, despite the large positive lattice dissociation energy. Thus, dissolution of some salts with multiply charged ions is energetically favorable, even though the salts have limited solubility.

Finally, there are pedagogical reasons why the traditional approach can be improved. There is a substantial body of evidence that students learn better in chemistry and other science classes that incorporate active learning.^{21–23} Traditional textbooks are not designed for a student-centered classroom environment, and instructors who want to experiment with alternative teaching strategies need other resources. The approach that we describe utilizes in-class activities in which students make observations about the solubility of molecular and ionic substances. Group worksheets help them to draw conclusions based on what they observed and to make the connections between macroscopic observations and molecular structure. Students are also guided to use standard thermodynamic data to help them explain solubility patterns.

■ NEW APPROACH TO PRESENTING SOLUBILITY

What Students Need To Understand about Dissolution

Because it is not possible to cover all aspects of this important topic in a first-year course, we have chosen to focus on exploring molecular explanations for the following observations:

- Polar substances generally dissolve in polar solvents such as water, whereas nonpolar substances do not.
- Some soluble substances dissolve exothermically and others endothermically.
- The solubility of ionic compounds varies with charge density.

Students should recognize that dissolution involves breaking and forming intermolecular attractions. We stress throughout the course that it takes energy to break “bonds”, and energy is released when new attractions form. Thus, energy is required to break solute–solute and solvent–solvent attractive forces. Similarly, energy is released as new attractions form when solute and solvent mix. The relative magnitudes of these energy terms determine whether the overall process is endothermic or exothermic. Many spontaneous processes move in the direction of lower energy, and students might expect that solutes will dissolve if, and only if, there is a net release of energy. However, they will observe that this is not the case: some substances dissolve readily even though energy must be absorbed from the surroundings, whereas other substances that are not very soluble release energy on dissolution. We want students to appreciate that energy considerations alone cannot predict which substances will dissolve and that other factors are involved.

When we discuss solutions in the first semester, we introduce the idea of entropy qualitatively so that students begin to understand that mixing inherently increases entropy. However, we also want students to appreciate the role that the entropy of water plays in solubility. When nonpolar molecules, or ionic compounds with multiply charged ions, dissolve in water there is an unfavorable net *decrease* in the entropy because the water molecules become more ordered than in the unmixed state. Thus, these substances are generally less soluble than polar molecules or ionic compounds with only singly charged ions, where the favorable increase in entropy due to mixing dominates.

In the second semester the concept of entropy is introduced more formally in terms of the number of distinguishable arrangements of the systems and surroundings. We know from observation that spontaneous events tend to go in one direction and not the other: solutions spontaneously mix, but do not “unmix”; heat flows from a hot body to a cold body and not vice versa, and so forth. Students use conceptual models to explore the processes of diffusion, osmosis, and heat transfer, and see that in each case the favored direction is the one that corresponds to an increase in the total number of arrangements (more formally microstates). They also calculate values for ΔH° (change in standard enthalpy), ΔS° (change in standard entropy), and ΔG° (change in standard free energy) for dissolution reactions and look for patterns that might help to explain why some substances dissolve and others do not. They discover that ion charge density (rather than the absolute charge on the ions) is the dominant factor in determining how the ions affect water.

Table 1. Summary of In-Class Activities Used To Introduce Concepts Related to Aqueous Solubility

activity ^a	subject	student observations	discussion focus
molecular solubility			
1	heat of dissolution of molecules	Temperature, T , increases when ethanol dissolves; T decreases when urea dissolves.	Energy cannot be the only factor determining solubility; entropy also plays a role.
2	molecular solubility	Methanol and ethanol are soluble; hexane is not; 1-butanol is slightly soluble.	Like dissolves like is useful but reorganization of water around nonpolar parts of molecules containing both polar and nonpolar regions decreases solubility.
ionic solubility			
3	heats of dissolution of ionic compounds	T increases when CaCl_2 dissolves; T decreases when KI dissolves.	The overall energy change depends on the relative magnitudes of the lattice and hydration energies.
4	solubility of ionic compounds	see Figure 4	Salts in which both the cation and anion are multiply charged are likely to be insoluble because the entropy of water decreases when it solvates multiply charged ions.
	exceptions	Silver halides are insoluble; many sulfates with multiply charged cations are soluble.	Exceptions have very positive or very negative energies of dissolution.
5	thermodynamics of ionic solubility	Solubility depends on the sign of ΔG . ^b Salts with only singly charged ions tend to have $\Delta S_{\text{dissolution}} > 0$ and multiply charged ions tend to have $\Delta S_{\text{dissolution}} < 0$.	In many cases, the sign of ΔS determines the sign of ΔG . Exceptions generally have very a large ΔH value, which overrides the sign of ΔS .

^aAll activities refer to aqueous solutions. ^bThe sign of ΔG determines the direction of any reaction. We use qualitative arguments in the first four activities to explore the relative importance of enthalpy and entropy as factors driving the dissolution process. See the sections on the roles energy and entropy for more details.

Finally, in addition to specific content, we stress the importance of using observations and data as the basis for reaching conclusions. We want students to understand that science is not static; our understanding changes as we gather more information. We also think that it is helpful that we as instructors make some connections between course material and current research in order to inform our own thinking about what is important to teach.

Overview of Our Approach

The approach that we describe is based on our experience using the ACS general chemistry textbook¹⁶ in our classes and on feedback from chemistry teachers at workshops that we have led. We introduce the topic of aqueous solubility with a series of in-class activities (Table 1). The first activity is completed after students have studied intermolecular forces of attraction (about week five of the first semester). On the basis of their own observations, students discover that some polar molecules dissolve with a net release of energy, whereas others absorb energy from the surroundings. This exercise makes it clear that the sign of the energy change alone cannot predict whether a substance will be soluble. At this point, we introduce entropy qualitatively as the other important factor in solubility. In the second activity, students observe that nonpolar substances are insoluble in water and discover that not all molecules that can hydrogen bond to water are soluble.

In activities 3 and 4, students explore the solubility of ionic compounds, which leads to a more general discussion of energy and entropy as the factors driving aqueous solubility. After entropy is introduced more formally in the second semester, students use energy and entropy data to calculate ΔH° , ΔS° , and ΔG° for dissolving ionic compounds (activity 5) and relate the values to structural features. Although these activities are designed for small groups working in class, they can also be done as demonstrations. Sample worksheets and instructor guides are included with the Supporting Information. Instructors can modify the worksheets (as we often do) to suit their curricula.

Role of Energy in Dissolution

Most general chemistry students have some experience with the idea that a decrease in energy accompanies many observable

processes, but we wish to enrich this understanding. We have also observed that students lack experience thinking about macroscopic phenomena at the molecular level. Thus, we try to address both of these issues early. In activity 1, students construct energy diagrams to analyze the changes that take place during solution formation using their observations of the temperature changes that accompany the dissolving process. Dissolution is modeled at the molecular level as a sequence of two steps. In the first step, individual solute particles are separated from each other, which is always an endothermic process as intermolecular forces of attraction are broken. In the second step, some water molecules are separated, and the solute and water are brought into contact to form the solution, which releases energy as new interactions are formed.^{24,25} The observable (net) energy change for dissolution can be represented as the sum of the energy changes for the two steps. Figure 1 shows an energy diagram that uses this model to represent endothermic dissolution. The net energy change, $\Delta E_{\text{dissolving}}$, represents the sum of the energy used to break solute–solute interactions ($\Delta E_{\text{sol-sol}}$) and the energy used to separate solvent molecules plus the energy released when new interactions form between solute and water ($\Delta E_{\text{hydration}}$). If $|\Delta E_{\text{sol-sol}}| > |\Delta E_{\text{hydration}}|$, as in this example, then $\Delta E_{\text{dissolving}} > 0$,

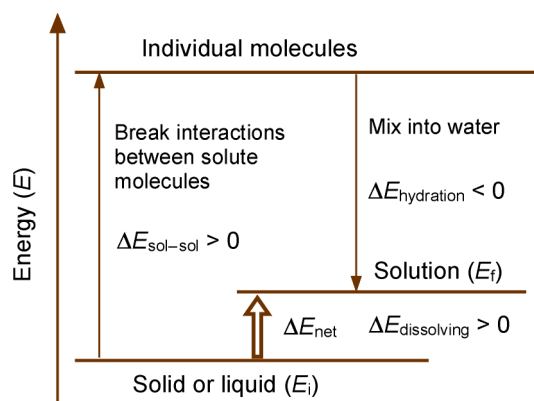


Figure 1. Energy diagram modeling the endothermic dissolution of a molecular compound in water (see text for explanation).

and the process is endothermic. This diagram makes it clear that in this case, the system is not going to a state of lower energy and that energy minimization cannot be the only factor driving dissolution. (Although it would be useful to explicitly include the energy needed to separate water molecules in the energy diagrams, there are no values available for this term as it is not known exactly how many water–water interactions must be broken. Because we want students to use the diagrams to calculate ΔE , we do not show a separate arrow for this process.) We use “energy”, a term students are familiar with, rather than enthalpy, as a simplification until we more formally introduce internal energy and enthalpy in the second semester.

When we turn our attention to ionic compounds, we build on the activities and ideas already described. In activity 3, students add solid potassium iodide or calcium chloride to water. They observe that the solution gets cold when KI dissolves and warm when dissolving CaCl_2 . Once again, we model the energy changes as the sum of two steps, first breaking interactions between ions (lattice dissociation energy) and then separating water molecules, which form new interactions with the ions (hydration energy). The lattice dissociation and hydration energies add to give the net energy: $\Delta E_{\text{dissolving}} = \Delta E_{\text{net}} = +2271 \text{ kJ mol}^{-1} - 2352 \text{ kJ mol}^{-1} = -81 \text{ kJ mol}^{-1}$ (Figure 2). The negative sign indicates that energy is

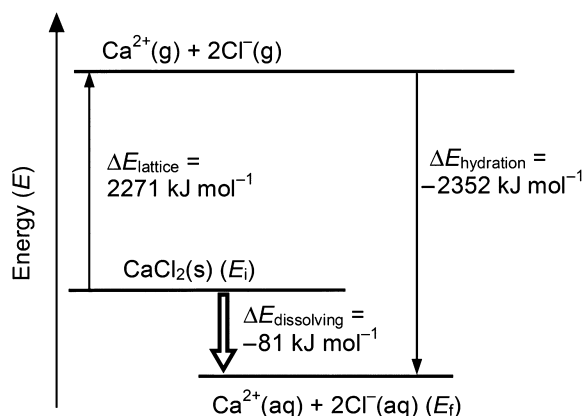


Figure 2. Energy diagram modeling the exothermic dissolution of CaCl_2 in water (not drawn to scale). See text for explanation.

released and explains why the solution feels warm upon mixing. Using this model, and their observations of the corresponding temperature changes, students conclude that the magnitude of the hydration energy for CaCl_2 must be greater than its lattice dissociation energy and that the reverse must be true for KI. Finally, we give students the appropriate data (Table 2) so that they can verify their conclusions and draw more accurate energy diagrams. The magnitudes of $\Delta E_{\text{lattice}}$ and $\Delta E_{\text{hydration}}$ are much larger for multiply charged ions compared to those of singly charged ions due to stronger Coulombic forces, but there is no pattern for $\Delta E_{\text{dissolving}}$ that can be used to predict solubility.

Role of Entropy in Dissolution

With a molecular view of the energy changes involved in dissolution in mind and an appreciation of the contribution of energy minimization in promoting molecular processes, we consider why in some cases dissolution occurs spontaneously even though an input of energy is required. To do this, we introduce the concept of entropy qualitatively in terms of the number of ways that the system can be arranged. The total

Table 2. Lattice Dissociation and Hydration Energies for a Few Common Ionic Salts

ionic compound	$\Delta E_{\text{lattice}}^a$ (kJ/mol)	$\Delta E_{\text{hydration}}^a$ (kJ/mol)	$\Delta E_{\text{dissolving}}^a$ (kJ/mol)
AgCl	918	−852	66
CaCl_2	2271	−2352	−81
CaCO_3	2811	−2822	−11
CaSO_4	2480	−2498	−18
CuSO_4	3066	−3139	−73
NaCl	790	−786	4
KI	650	−631	19

^aThe energy refers to enthalpy (see text for explanation). Data from ref 26.

number of ways that the particles (solute and water) can be arranged increases with mixing, which makes the mixed state more probable than the unmixed state. As a result, mixing corresponds to an increase in the entropy of the system. Because first-year students are not ready for a more sophisticated statistical mechanical description of entropy, we refer to particles spreading out as “positional entropy increase”, which is relatively easy for students to understand. The idea that mixing plays an important role in dissolution is consistent with students’ own experience that solutions never spontaneously unmix, so it is intuitive that molecular processes tend toward a mixed state. In some cases, this entropy increase is large enough to compensate for the unfavorable requirement that energy must be added, and when this happens, the solute dissolves.

Nevertheless, the increase in entropy with mixing cannot explain why some substances do not dissolve. Students must also consider the role of water reorganization during dissolution. For example, in activities 1 and 2 students discover that methanol, ethanol, and urea dissolve in water, whereas hexane does not, which implies that solutes that can hydrogen bond with water will be soluble. However, the relative insolubility of 1-butanol is counter-evidence, because 1-butanol can form as many hydrogen bonds with water as ethanol. This observation suggests that the larger nonpolar portion of 1-butanol is responsible for the lower solubility. It is a decrease in the entropy that arises from a shell of water molecules arranged in a fixed orientation around the nonpolar hydrocarbon end of 1-butanol that makes it insoluble.^{27–29} Figure 3 shows a sketch of a few of the hydrating water molecules oriented around 1-butanol in a way that keeps one hydrogen available to hydrogen

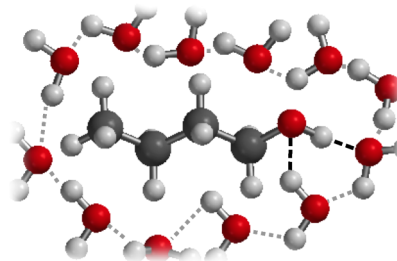


Figure 3. Shell of water molecules effectively surrounding the nonpolar hydrocarbon chain of 1-butanol (only a single plane of the whole three-dimensional sphere is shown). The short dashes show hydrogen bonding between water molecules surrounding the nonpolar hydrocarbon chain. The two dark dashed lines show dynamic hydrogen bonding to the hydroxyl group of the alcohol.

bond with bulk water. The decreased entropy of the water is greater than the increase in entropy due to solute–solvent mixing, which makes 1-butanol insoluble. The primary reason why nonpolar molecules do not dissolve in water is because the movement of water molecules near the solute becomes too restricted compared to the dynamic motions in pure water.

■ A CLOSER LOOK AT ENERGY AND ENTROPY CHANGES FOR DISSOLVING IONIC COMPOUNDS

Simple Solubility Rule for Ionic Compounds

Now we turn to an in-depth discussion of activities 4 and 5, which focus on the solubility of ionic compounds. Before students can think about factors that might explain differences in solubility, they need to have a more complete picture of which salts are soluble and which are not. In activity 4, they mix different pairs of ionic salts in order to see which ion combinations produce insoluble products and which products remain in solution. They then determine the identity of each insoluble precipitate by the process of elimination. Figure 4

	KNO ₃	KBr	K ₂ CO ₃	K ₂ C ₂ O ₄	K ₃ PO ₄
NaCl					
CaCl ₂			PPT	PPT	PPT
CoCl ₂			PPT	PPT	PPT
ZnCl ₂			PPT	PPT	PPT

Figure 4. Grid of ionic precipitation reactions used to deduce essential solubility rules. The columns contain different anions, each as a potassium salt, and the rows contain cations as chloride salts.

shows a typical grid for this activity along with the expected results. Four ion combinations, including the two starting compounds, are possible in each cell. The starting compounds are known to be soluble, so by looking at the possible combinations in cells with no precipitate, students can deduce the identities of the precipitates (PPT). For example, in the cell containing CaCl₂ and K₃PO₄, KCl and Ca₃(PO₄)₂ are possible

precipitates. However, KCl is a possible combination in all cells in the first row, none of which show a precipitate, so KCl must be soluble and the precipitate must therefore be Ca₃(PO₄)₂. As the students look for features that distinguish the insoluble salts from those that are soluble, they discover a simple solubility “rule” that predicts results correctly in most cases: *Ionic compounds in which both the anion and the cation are multiply charged are likely to be insoluble; other salts are likely to be soluble.* (The starting solutions in this activity are deliberately chosen so that exceptions to this simple rule are encountered only after the rule has been articulated.) In addition to its simplicity, this approach focuses students’ attention on the role of ionic charge, which gets lost when solubility is presented as a list of rules.

Dissolving Compounds with Multiply Charged Versus Singly Charged Ions

Salts with multiply charged ions are less likely to be soluble than salts with only singly charged ions. This is generally explained by the greater strength of the interactions between multiply charged ions, which makes it harder for the ions to separate. When students are asked how this assumption would be reflected in the energy diagrams (Figure 2) for dissolving the salts, they predict that the lattice dissociation energies for salts with multiply charged ions should be greater than the lattice energies for salts with only singly charged ions, which would make the net energy change for dissolving the multiply charged salts unfavorable. We then have them test this hypothesis by giving them values for lattice and hydration energies. These data show that the lattice energies are indeed larger when multiply charged ions are present because of the stronger ion–ion attractions. For example, the lattice energies for NaCl, CaCl₂, and CaCO₃ are 790, 2271, and 2811 kJ mol^{−1}, respectively (Table 2). However, the hydration energies are also greater when multiply charged ions are involved, as these ions also attract water more strongly; the values of $\Delta E_{\text{hydration}}$ for the same three salts are −786, −2352, and −2822 kJ mol^{−1}. Despite the fact that the lattice energy for CaCO₃ is quite large, the net energy change for dissolving CaCO₃ is actually

Table 3. Enthalpy, Entropy, and Gibbs Energy Values for Illustrative Aqueous Ionic Dissolution Reactions

reaction	dissolution equation	$\Delta H^\circ/\text{kJ}^\text{a}$	$\Delta S^\circ/(\text{J K}^{-1})^\text{a}$	$\Delta H^\circ - T\Delta S^\circ = \Delta G^\circ/\text{kJ}^\text{a}$
1	$\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$	65.8	33.8	55.7
2	$\text{AgNO}_3(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$	23.3	79.2	−0.3
3	$\text{KF(s)} \rightleftharpoons \text{K}^+(\text{aq}) + \text{F}^-(\text{aq})$	−18.9	20.8	−25.1
4	$\text{KCl(s)} \rightleftharpoons \text{K}^+(\text{aq}) + \text{Cl}^-(\text{aq})$	16.7	75.1	−5.7
5	$\text{KBr(s)} \rightleftharpoons \text{K}^+(\text{aq}) + \text{Br}^-(\text{aq})$	18.6	87.3	−7.4
6	$\text{KI(s)} \rightleftharpoons \text{K}^+(\text{aq}) + \text{I}^-(\text{aq})$	18.7	101.2	−11.4
7	$\text{LiCl(s)} \rightleftharpoons \text{Li}^+(\text{aq}) + \text{Cl}^-(\text{aq})$	−37.3	9.6	−40.1
8	$\text{NaCl(s)} \rightleftharpoons \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$	3.6	42.7	−9.1
9	$\text{NaClO}_4(\text{s}) \rightleftharpoons \text{Na}^+(\text{aq}) + \text{ClO}_4^-(\text{aq})$	14.3	100.2	−15.5
10	$\text{NH}_4\text{Cl(s)} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$	14.1	73.2	−7.7
11	$\text{CaCl}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$	−81.4	−47.6	−67.2
12	$\text{Na}_2\text{CO}_3(\text{s}) \rightleftharpoons 2\text{Na}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$	−25.0	−69.1	−4.4
13	$\text{Na}_2\text{SO}_4(\text{s}) \rightleftharpoons 2\text{Na}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$	−5.5	−14.1	−1.3
14	$\text{MgBr}_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{Br}^-(\text{aq})$	−185.5	−89.1	−159.0
15	$\text{MgCO}_3(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$	−46.4	−252.7	28.9
16	$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$	−11.3	−199.1	48.0
17	$\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$	26.2	−104.1	57.2
18	$\text{CaSO}_4(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$	−18.2	−144.4	24.8
19	$\text{CoSO}_4(\text{s}) \rightleftharpoons \text{Co}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$	−79.2	−212.5	−15.9
20	$\text{CuSO}_4(\text{s}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$	−73.1	−188.3	−17.0

^aData from refs 34 and 35

favorable ($\Delta E^\circ < 0$), so the low solubility of CaCO_3 cannot be attributed to an energy effect at all. Students are reminded that the reorganization of the water molecules must also be taken into account. The stronger attraction between the multiply charged ions and the water, $\Delta E_{\text{hydration}}$, limits the motion of many hydrating water molecules, resulting in an unfavorable decrease in entropy.

Once the students have formulated their rule, they use it to predict the solubility of other ionic compounds. Although they will predict the results for most salts correctly, they also discover that there are exceptions to the simple pattern; in particular, the silver halides are less soluble than expected, whereas many sulfates, including CoSO_4 and CuSO_4 are more soluble. When the students compare the lattice and hydration energies of the silver halides to the values for similar salts that are soluble, they see that the net energy for dissolving silver halides is especially unfavorable. For example, the net energy change for dissolving AgCl is 66 kJ mol^{-1} , whereas ΔE for dissolving NaCl is 4 kJ mol^{-1} (Table 2). (In fact, the lattice dissociation energy for AgCl , 918 kJ mol^{-1} , is larger than would be expected for a purely ionic bond. It has been suggested that this is evidence for covalent bonding in the AgCl crystal structure, which contributes to its low solubility.^{30–33}). Similarly, soluble sulfates have large, negative ΔE values compared to salts that are insoluble, which makes these sulfates more likely to dissolve. In general, unusually large energy changes account for exceptions to our simple solubility rule.

Using Thermodynamics To Explore Solubility Patterns

Students return to the question of solubility in the second semester (activity 5), after they have learned about enthalpy, entropy, and Gibbs free energy. They calculate ΔH° and ΔS° for dissolving a number of salts with data from standard thermodynamic tables and use their results to compute ΔG° for the dissolution process. (See Table 3 for typical results.) The students look for correlations between the thermodynamic values and solubility of the salts and recognize that it is the sign of ΔG° that determines whether a salt will dissolve, consistent with what they have recently learned about spontaneity. Next, they look to see how salts with at least one multiply charged ion (reactions 11–20 in Table 3) differ from salts with only singly charged ions (reactions 1–10) and how salts with *two* multiply charged ions (reactions 15–20) compare to those with only one (reactions 11–14). They discover that although both ΔH° and ΔS° play a role in determining overall solubility, the entropy term better correlates with the simple solubility rule that they discovered earlier. For example, for salts with only singly charged ions, $\Delta S^\circ_{\text{dissolving}}$ is almost always “favorable” (i.e., $\Delta S^\circ > 0$, which makes it more likely that ΔG° will be < 0). Thus, salts with only singly charged ions are almost always soluble; exceptions are salts with unusually large, positive ΔH° values, such as AgCl . When multiply charged ions are present, $\Delta S^\circ_{\text{dissolving}}$ is almost always negative. In the case of salts with one multiply charged ion, the magnitude of ΔS° is generally relatively small so that as long as $\Delta H^\circ < 0$, the salt is still likely to be soluble. However, when both ions are multiply charged, the entropy term is much more negative, and therefore the salt will only be soluble if there is an unusually large negative ΔH° .

Although there is no similar correlation between enthalpy and ion charge, in a few cases, the magnitude of ΔH° is large enough to make the enthalpy change the determining factor in solubility. As noted earlier, ΔH° for dissolving many sulfates is

unusually large and negative so that $\Delta G^\circ < 0$ despite the negative value for ΔS° . Similarly, we have already seen that ΔH° for dissolving silver halides is unusually large and positive so that $\Delta G^\circ > 0$ despite their favorable ΔS° values. Note that in both of these cases, the ΔS° values for dissolution are consistent with the ΔS° values for similar salts: for AgCl , the value of ΔS° is positive, like that of other $+1/-1$ salts. Similarly, ΔS° values for dissolving CuSO_4 and CoSO_4 are large and negative, like those for other $+2/-2$ salts (Table 3). Thus, it is the magnitude of ΔH° that makes these salts exceptions to the solubility rule.

Role of Charge Density

Finally, in order to explore factors other than ion charge that might affect the entropy of dissolution, students are asked to make a prediction about ΔS° for dissolving LiF . Not surprisingly, they expect that because only singly charged ions are present ΔS° for LiF will be positive, and the salt will be soluble. Because the solubility is actually quite low, they are asked to think about what might distinguish LiF from other $+1/-1$ salts. This leads them to explore the effect of ionic size. The series KCl , NaCl , and LiCl reveals that decreasing the radius of the cation causes ΔS° to become less favorable (i.e., less positive) and ΔH° to be more favorable.^{4,28,36,37} Decreasing the radius of the anion (as in the series KI , KBr , KCl , and KF) has the same effect. This leads students to reason that ΔS° for dissolving LiF should be less favorable than for either LiCl or KF . In fact, the value of ΔS° for dissolving LiF is $-37.3 \text{ J mol}^{-1} \text{ K}^{-1}$, confirming that ion size does affect the entropy of dissolution.

Although it is not easy to separate the effects of ion charge from the effects of ion size, a comparison of ΔS° for dissolving CaSO_4 and NaClO_4 confirms that it is not ion size alone that matters. The aqueous radii of Ca^{2+} (103 pm) and Na^+ (97 pm) are similar, as are the radii of ClO_4^- (241 pm) and SO_4^{2-} (242 pm).³⁸ However, ΔS° for dissolving CaSO_4 ($-144 \text{ J mol}^{-1} \text{ K}^{-1}$) is much less favorable than for dissolving NaClO_4 ($+100 \text{ J mol}^{-1} \text{ K}^{-1}$), showing that charge must also be considered to explain the differences in the entropy of dissolution for these two salts. The charge density of the ion takes both of these factors into account. A higher charge density results in stronger Coulombic attractions between the ion and the hydrating water molecules, which increases the extent of ordering of the water. As more water molecules are involved in hydrating the ions, $\Delta S_{\text{hydration}}$ becomes more negative.³⁹ If enough water molecules lose freedom of motion (relative to pure water) as they surround the dissolving ions, solubility will decrease³⁹ as the entropy of hydration $\Delta S_{\text{hydration}}$ becomes more negative. The number of water molecules needed to hydrate an ion depends in part on the charge density; in this case, the doubly charged Ca^{2+} ion is hydrated by relatively more water molecules than singly charged Na^+ . Figure 5 illustrates that more water molecules are arrayed around Ca^{2+} compared to Na^+ , which results in a decrease in entropy relative to bulk water.

Lithium, sodium, and potassium ions all have the same charge, but because lithium ions are smaller, they have a larger charge density. Similarly, fluoride ions have a greater charge density than the other halide ions. Because lithium fluoride combines two ions with high charge density, the entropy of dissolution is unfavorable.

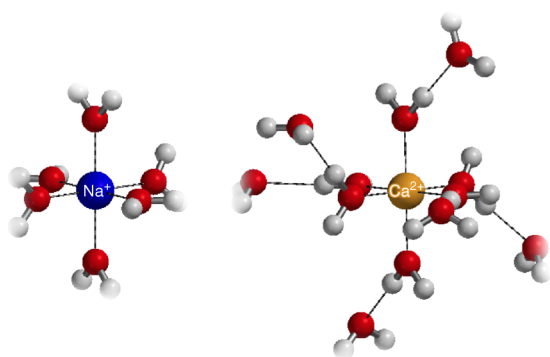


Figure 5. Hydration spheres of two cations with similar radii but different charges are compared pictorially. These pictures are representative because the number and arrangement of water molecules is dynamic and not precisely known.

■ CONNECTIONS TO RESEARCH ON THE STRUCTURE OF WATER

Although most general chemistry students will not be interested in details about current research on water structure, some students are curious about this and we try to share our interest. The structure of pure water and the interaction between water molecules and solutes remain intense areas of research. Pure water is hydrogen bonded, but recent research shows that the average number of hydrogen bonds is lower than previously thought.^{40–43} In addition, the hydrogen-bonding network is dynamic, with individual molecules forming and breaking hydrogen bonds rapidly. Most of the research on water structure in solutions relates to the water molecules nearest the solute. Some substances, such as butanol and Mg^{2+} (known as kosmotropes), cause water to become more ordered when they dissolve, whereas others including urea and Na^+ (chaotropes) have the opposite effect. The corresponding decrease or increase in the entropy of the water dominates the overall entropy change for the dissolution process, but the exact nature of “water ordering” remains ambiguous.

For ionic solutes, Dill et al.²⁸ modeled what happens when water surrounds ions that have the same charge but differ in size and concluded that small ions reorder water molecules via strong dipole–dipole interactions between the ion and a hydration layer of water. This fixes the water molecules in a single orientation, which decreases the entropy and makes small ions less soluble. In the presence of large ions, most water molecules exist in a dynamic hydrogen-bonded network. Although the trends in water ordering are the same for cations and anions, the charge density of anions affects the solvation sphere of water more strongly.^{4,28,44} For example, F^- and Rb^+ are both singly charged ions with radii close to 1.5 Å, but the entropy of solvation for F^- is negative, whereas it is positive for Rb^+ . One important difference between the interactions of water with cations and anions arises from the asymmetry of water’s dipole moment. Anions can get closer to the positively charged hydrogen atoms, which are positioned on the surface of the water molecule, whereas cations interact with oxygen in the center of a water molecule. The shorter interaction distance of anions makes anions interact more strongly than cations given similar charge densities.

The decreased entropy of water in the presence of nonpolar solutes is not due to strong attractions for the solute, as it is for ions. Instead, the usual explanation involves the formation of clathrate-like structures.^{9,28} In another model, Wallqvist and

Covell focus on the cavity size in solvents.⁴⁵ Water is a relatively small molecule that packs tightly. The tight packing means that there are relatively few cavities available for solute molecules, which lowers the probability of solvation and, therefore, the entropy and overall solubility. They conclude from their modeling studies that about two-thirds of the hydrophobic effect is due to size considerations.

Although we do not present this material in detail to our general chemistry students, we believe it is important to remember that chemistry is not a static subject and that even with such a fundamental topic, there is still much to study.

■ WHY THIS APPROACH IS AN IMPROVEMENT

We believe that our approach as described in this paper is an improvement over the way that solubility is traditionally presented in general chemistry in terms of both content and pedagogy. Formulating a solubility rule based on ion charge makes it easier to see connections between microscopic structure and macroscopic behavior. The emphasis is on using observation and data to reach conclusions so that students are actively engaged in a process akin to scientific research. Science is always subject to revision as a result of new research, and this approach emphasizes reasoning skills that can be applied to new situations and future discoveries. The expanded treatment of entropy allows a more balanced presentation of the roles of energy and entropy in solution formation. Research in all of the major subdisciplines of chemistry relies on entropy and energy to explain such diverse topics as protein folding,^{46,47} water-filled carbon nanotubes,⁴⁸ activated complexes in mechanisms,^{49,50} and binding reactions.^{51–53} Textbooks necessarily evolve with current research, and we feel that the substantial body of literature on the importance of entropy in explaining chemical phenomena justifies a parallel shift in our teaching.

■ ASSOCIATED CONTENT

§ Supporting Information

Sample worksheets and instructor guides. This material is available via the Internet at <http://pubs.acs.org>.

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Notes

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