

The Solubility Rules: Why Are All Acetates Soluble?

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Solubility rules for inorganic compounds in aqueous solution are taught in most introductory college and high school courses. These rules are simple enough for most students to memorize and in some cases apply to laboratory exercises such as qualitative analysis schemes (1). The solubility rules in the text used in our 1998–99 introductory course are summarized below (2).

Solubility Rules for Ionic Compounds in Water

Soluble Salts

Group 1 cations and NH_4^+ ions form soluble salts.

All nitrates are soluble.

Most halides are soluble, with the exceptions of those of Pb^{2+} , Hg_2^{2+} , Ag^+ , and Cu^+ .

Most sulfates are soluble, with the exceptions of those of Ba^{2+} , Sr^{2+} , and Pb^{2+} , Ag^+ , Ca^{2+} , and Hg_2^{2+} form slightly soluble sulfates.

Insoluble Salts

Hydroxides, oxides, and sulfides are usually insoluble, except that those of group 1 ions and NH_4^+ are soluble and those of group 2 ions are slightly soluble.

Chromates, phosphates, and carbonates are usually insoluble, except that those of group 1 ions and NH_4^+ are soluble.

One of my senior colleagues recently suggested that we add the rule “all acetates are soluble”. This “new” rule (3, 4) took me by surprise and I immediately and naively challenged it, on the basis that acetate is a weak base and should form insoluble compounds in combination with acidic cations having high

charge densities. I would like to present a discussion of the thermodynamic arguments that formed the basis of my objections (5, 6).

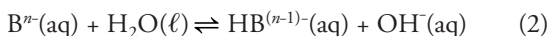
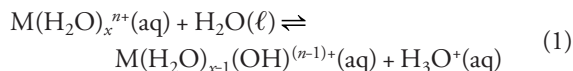
This paper is the result of a semester-long discussion/debate that eventually broadened to include an inorganic, an analytical, and two organic chemistry professors as well as several undergraduate students ranging from seniors to freshmen. The students were enrolled in a variety of courses, from introductory to physical and advanced inorganic chemistry. In retrospect we realized that this effectively engaged these students in a high-level scientific discussion that produced a very stimulating academic environment. We hope to continue this approach and perhaps even institutionalize it in the form of a seminar course for highly motivated students as part of our honors program. We were particularly thrilled by the interactions of our upperclassmen with the introductory students in a team environment. In the future this would involve selecting a topic from our introductory course that the textbook has presented with little or no substantiation and having the students help research and defend positions on that topic.

The material discussed in this paper could also be incorporated into more traditional curricula, into an honors introductory chemistry course, or into physical chemistry and advanced inorganic chemistry. However, this material is probably *not* easily incorporated into a traditional introductory chemistry course, owing to the breadth and sophistication of the concepts involved.

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Discussion

The three general types of ions in aqueous solution are (i) nonacidic cations and nonbasic anions that do not undergo hydrolysis; (ii) acidic cations that undergo hydrolysis (eq 1); and (iii) basic anions that undergo hydrolysis (eq 2).



There are four possible combinations of cation and anion types that result in either soluble or insoluble compounds (7). The overall solubilities of ionic solids appear to be dependent upon the acid–base properties of the component cations and anions. The following generalizations concerning the solubilities of ionic compounds can be made: (i) if both the cation and the anion undergo hydrolysis, then the compound will usually be insoluble, and (ii) if one or both of the ions do not undergo acid–base hydrolysis, then the compound is usually soluble.

Table 1 lists thermodynamic data for selected precipitation reactions. To summarize these data:

1. *Acidic cations and basic anions.* Combinations of these ions generally produce spontaneous precipitation due to the insolubility of the resulting neutral ionic compounds. These combinations can be either exothermic or endothermic and precipitation is generally entropically driven by the $-T\Delta S^\circ$ term in ΔG° .
2. *Nonacidic cations and basic anions or acidic cations and nonbasic anions.* These combinations usually do not result in precipitation. The precipitation reactions are highly endothermic, with near neutral or slightly negative $-T\Delta S^\circ$ contributions to free energy changes.
3. *Nonacidic cations and nonbasic anions.* While these combinations usually do not result in precipitation, the resulting compounds are not nearly as soluble as one would expect based on the simple rule that nonacidic or nonbasic ions form soluble compounds. It might be expected that if ionic compounds with one nonacidic or one nonbasic ion are soluble, two of these ions should produce even more solubility. This is not the case. These precipitation reactions are usually exothermic, but are entropically unfavorable, the two opposing terms resulting in near zero free energies. Precipitation is determined by whether the difference $\Delta H^\circ - T\Delta S^\circ$ is significantly less than zero.

The Entropy Term

The reaction of an acidic cation such as Zn^{2+} with a basic anion such as S^{2-} results in precipitation (eq 3) primarily due to a positive entropy term. At first glance this may seem counterintuitive, since the reaction appears to be creating a more ordered state by going from ions in solution to the solid and thus reducing the number of species, going from reactants (two ions) to products (one compound).

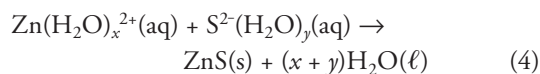


We must not forget, though, that ions in aqueous solution are hydrated, bonded to water molecules. From a thermodynamic point of view it would be more appropriate to write this

Table 1. Data at 298 K for Precipitation Reactions of Ionic Compounds (8)

Ionic Compound	$\Delta G_{298}^\circ / (\text{kJ mol}^{-1})$	$\Delta H^\circ / (\text{kJ mol}^{-1})$	$-T\Delta S_{298}^\circ / (\text{kJ mol}^{-1})$	$\text{p}K_{\text{sp}}$
<i>Acidic Cations and Basic Anions</i>				
$\text{Fe}(\text{OH})_3$	-221	-85	-136	38.8
CuCO_3	-55	470	-525	9.63
FeCO_3	-61	519	-580	10.68
$\text{Pb}_3(\text{PO}_4)_2$	-248	1934	-2182	43.53
CuS	-205	-151	-54	36.1
MnS	-77	139	-216	13.5
<i>Nonacidic Cations and Basic Anions</i>				
Na_2S	88	82	6	-15.42
NaOH	50	45	5	-8.76
KOH	62	58	4	-10.8
K_2CO_3	28	30	-2.2	-4.91
KF	25	18	7	-4.38
<i>Acidic Cations and Nonbasic Anions</i>				
$\text{Mg}(\text{NO}_3)_2$	89	85	4	-15.6
$\text{Mg}(\text{ClO}_4)_2$	144	141	4	-25.24
AlCl_3	253	330	-77	-44.34
FeCl_3	64	150	-86	-25.83
<i>Nonacidic Cations and Nonbasic Anions</i>				
NaCl	9	-4	13	-1.5
NaClO_4	15	-14	29	-2.63
NaNO_3	3	-23	26	-0.53
KBr	5	-21	26	-0.88
KI	11	-21	32	-1.93
CsClO_4	-12	-55	44	2.10
KClO_4	-12	-52	40	2.10

reaction including the waters of hydration (eq 4).



In fact, the greatest numbers of hydrated water molecules are bound by the most acidic cations and most basic anions (Table 2). The number of water molecules involved in forming a hydrated ion is dependent upon the charge density of the ion. These water molecules can form two distinct layers, the first having water molecules that are directly interacting with the ion and a second involving hydrogen bonding of water molecules to those in the first layer. This hydrogen bonding can be enhanced by the polarization of electrons imposed by the charge of the ion and is distinctly different from that observed in the bulk water. Large ions with low charge densities have only a small influence on water molecules in the second layer, whereas small ions with high

Table 2. Hydration Numbers for Selected Cations (9)

Ion	$(Z^2/r)/\text{\AA}^{-1}$ ^a	Hydration Number
Cs^+	0.55	6
K^+	0.66	7
Na^+	0.86	13
Li^+	1.1	22
Cd^{2+}	3.7	39
Zn^{2+}	4.5	44

^a Z is the charge of the ion and r is the radius, as in Coulomb's law.

Table 3. A Comparison of the Thermodynamics of Precipitation to Lattice and Hydration Energies of Ionic Solids

Compound	Crystal Structure Type	$-T\Delta S_{\text{ppt}}/$ (kJ mol ⁻¹)	$\Delta H_{\text{ppt}}/$ (kJ mol ⁻¹)	$U_{\text{lat}}/$ (kJ mol ⁻¹)	$\Sigma \Delta H_{\text{hyd}}/$ (kJ mol ⁻¹)
NaCl	NaCl	13	-4	787	-783
AgCl	NaCl	10	-66	915	-850
TlCl	CsCl	21	-43	749	-706
KF	NaCl	7	18	827	-844
NaF	NaCl	-2	-1	928	-927
LiF	NaCl	-11	-82	1046	-964
CoCl ₂	CdCl ₂	-32	79	2691	-2770
PbCl ₂	PbCl ₂	-4	-23	2266	-2243

Table 4. Lattice Energies of Acetates and Hydration Energies for the Cations

Compound	Lattice Energy/ (kJ mol ⁻¹)	Ion	$\Delta H_{\text{hyd}}^{\circ}/$ (kJ mol ⁻¹)
NaO ₂ CCH ₃	763	Na ⁺	-405
KO ₂ CCH ₃	682	K ⁺	-321
RbO ₂ CCH ₃	656	Rb ⁺	-296
AgO ₂ CCH ₃	863	Ag ⁺	-475
TlO ₂ CCH ₃	750	Tl ⁺	-326
Ca(O ₂ CCH ₃) ₂	2294	Ca ²⁺	-1592
Sr(O ₂ CCH ₃) ₂	2166	Sr ²⁺	-1445
Ba(O ₂ CCH ₃) ₂	2033	Ba ²⁺	-1304
Cu(O ₂ CCH ₃) ₂	2835	Cu ²⁺	-2100
Zn(O ₂ CCH ₃) ₂	2750	Zn ²⁺	-2044
Pb(O ₂ CCH ₃) ₂	2225	Pb ²⁺	-1480

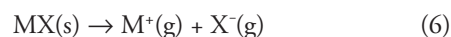
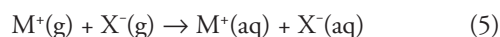
charge densities exert a large influence on the number of water molecules in the second layer. Highly hydrated ions release the greatest number of water molecules into solution upon forming a precipitate. The generation of many more independent products than reactants offsets the unfavorable change in state of the ions themselves and results in a large positive entropy term.

For the reaction of an acidic cation with a nonbasic anion, or a basic anion with a nonacidic cation, one of the species is extensively hydrated. There is a more limited ability to overcome the unfavorable change in state of the ions and the $-T\Delta S^{\circ}$ term does not make a significant negative contribution to the free energy change. Finally, the reaction of nonacidic cations with nonbasic anions is entropically unfavorable owing to the change of state from ions in solution to the crystalline solid. Nonacidic and nonbasic ions are not extensively hydrated and release few water molecules upon formation of a precipitate.

The Enthalpy Term

We must understand the factors that influence the enthalpy of precipitation; however, one is much more likely to find values for heats of solution in the literature. The Born–Haber approximation allows us to separate heats of solution into two components, heats of hydration of ions and the lattice

energy of the solid. By convention, hydration energies (ΔH_{hyd}) are negative, defined as making the bonding interactions between the water molecules and ions in solution (eq 5). Lattice energies (U_{lat}) are positive (9), defined as breaking the ionic bonding interactions in the solid state (eq 6). Since precipitation (eq 7) is the reverse of dissolution, the enthalpy of precipitation (ΔH_{ppt}) is the negative of the heat of solution. Therefore, ΔH_{ppt} is the negative of the sum of the hydration energies plus the lattice energy (eq 8).¹



$$\Delta H_{\text{ppt}} = -(\Delta H_{\text{hyd}} + U_{\text{lat}}) \quad (8)$$

The relative magnitudes of the hydration energies of the ions and the lattice energy of a solid are a very important consideration in understanding solubility. This is especially true for insoluble compounds that are exceptions to the solubility rules. Table 3 compares the hydration and lattice energies of some relevant soluble and insoluble compounds.

The large lattice energies of the insoluble compounds tip the scale in favor of precipitation. This extra lattice energy (compared to that of the soluble compounds) arises from differences in the interactions of the cations and anions in the crystalline solids (11). For example, if the size of the cation closely matches the size of the hole in a close-packed anion structure, an increase in lattice energy will result. As Pauling stated, “The simplicity of the theory is due in part to the importance in the interionic interactions of the well understood Coulomb terms, and in part to the spherical symmetry of the electron distributions of the ions with noble-gas or eighteen-shell configuration.” However, while charge interactions are often the dominant factor in lattice energies, they are not the only factor. As Wulfsberg points out (5, p 214), AgBr adopts the NaCl structure, yet calculations of the lattice energy of AgBr using the coulombic model results in unsatisfactory agreement with experimental values. This is presumably due to the increased electronegativity and polarizability of Ag⁺ as compared with Na⁺, and the resulting increased covalent interactions between the cation and anion in the solid state (12).

Why Are Most Acetates Soluble?

So where do acetates fall in the grand scheme of things? Based on the foregoing discussion and the fact that acetate is a weak base, a relatively brash young professor² might predict that in combination with acidic cations, an anion such as acetate should form insoluble compounds. In fact, this is not the case. Most acetates are soluble, Ag⁺ (13) and Fe³⁺ (1) being the only exceptions cited in the literature.

To resolve this conundrum we had to find the appropriate thermodynamic data. To determine the enthalpy of precipitation for acetates we needed to find the lattice energies and hydration energies for a variety of acetate salts. It was easy enough to find both the lattice energies of a variety of acetates (8b) and the hydration energies of cations (Table 4) (5), but we were unable to find the hydration energy of acetate. Enthalpies of solution can also be calculated from the enthalpies of formation of the solid and aqueous species (Table 5). The data for sodium acetate seemed to be consistent with the category

Table 5. Thermodynamic Data for Acetate Salts

Formula	$\Delta H_f^\circ(\text{aq})/$ (kJ mol ⁻¹)	$\Delta H_f^\circ(\text{s})/$ (kJ mol ⁻¹)	$\Delta H_{\text{ppt}}^\circ/$ (kJ mol ⁻¹)	$S^\circ(\text{aq})/$ (J mol ⁻¹ K ⁻¹)	$S^\circ(\text{s})/$ (J mol ⁻¹ K ⁻¹)	$\Delta S_{\text{ppt}}^\circ/$ (J mol ⁻¹ K ⁻¹)	$-T\Delta S_{\text{ppt}}^\circ/$ (kJ mol ⁻¹) (298 K)	$\Delta G_{\text{ppt}}^\circ/$ (kJ mol ⁻¹) (298 K)
NaO ₂ CCH ₃	-726	-709	17	146	123	-23	7	24
KO ₂ CCH ₃	-738	-723	15	189	—	—	—	—
AgO ₂ CCH ₃	-380	-399	-18	159	150	-10	3	-15
TlO ₂ CCH ₃	-481	-528	-47	212	—	—	—	—
Cu(O ₂ CCH ₃) ₂	-907	-893	14	74	—	—	—	—
Zn(O ₂ CCH ₃) ₂	-1118	-1079	39	—	—	—	—	—
Ba(O ₂ CCH ₃) ₂	-1510	-1485	25	183	—	—	—	—
Pb(O ₂ CCH ₃) ₂	-853	-879	-26	183	—	—	—	—
Ca(O ₂ CCH ₃) ₂	-1515	-1480	35	120	—	—	—	—

of nonacidic cation and basic anion. Likewise, everything seems to be in order for silver acetate; that is, both the ΔH and $-T\Delta S$ terms are more negative for the Ag⁺ ion than for the Na⁺ ion owing to the increased electronegativity of silver. Unfortunately, entropy data are not available for acetates of the acidic cations such as Cu²⁺ and Zn²⁺, but the enthalpies of precipitation are only modestly endothermic.

At this point the only missing piece of the puzzle was the hydration energy of acetate, and I was sure that the answer would be revealed if this datum were available. Fortunately, we have all the data necessary to calculate the hydration energy of acetate using eq 8, namely the precipitation enthalpy

Table 6. Calculated Hydration Enthalpy of Acetate

Calculated from	$\Delta H_{\text{hyd}}^\circ/$ (kJ mol ⁻¹)
NaO ₂ CCH ₃	-375
KO ₂ CCH ₃	-376
AgO ₂ CCH ₃	-370
TlO ₂ CCH ₃	-377
Cu(O ₂ CCH ₃) ₂	-375
Zn(O ₂ CCH ₃) ₂	-372
Ba(O ₂ CCH ₃) ₂	-377
Ca(O ₂ CCH ₃) ₂	-369
Pb(O ₂ CCH ₃) ₂	-360

Table 7. Hydration Enthalpies and Aqueous pK_b Values for Selected Anions

Ion	$\Delta H_{\text{hyd}}^\circ/$ (kJ mol ⁻¹)	pK _b
CH ₃ CO ₂ ⁻	-374	9.24
HCO ₂ ⁻	-384	10.25
NO ₂ ⁻	-383	10.85
F ⁻	-497	10.83
Cl ⁻	-355	14
Br ⁻	-328	14
I ⁻	-287	14
NO ₃ ⁻	-370	14

($\Delta H_{\text{ppt}}^\circ$), the lattice energy (U_{lat}), and the hydration energy of the cations for several acetate salts. The only unknown left in the equation is the hydration energy of acetate. Table 6 lists the calculated hydration energy of acetate derived from the available data, which give a mean value of -372 ± 4 kJ/mol.³ Table 7 compares the pK_b and hydration energies of acetate to those of the halides. Although acetate is a stronger base than fluoride, its hydration energy is considerably less negative than fluoride's and only slightly more negative than that of chloride. Could it be that simple? Acetate behaves more like a nonbasic anion than a basic anion, which is consistent with the proposed solubility rule "all (or most) acetates are soluble".

Probably every organic chemist reading this paper is champing at the bit, ready to scream out the obvious answer to the problem: "Acetate is an organic ion, not an inorganic ion!" That methyl group changes everything. The degree

of hydration in solution is influenced by the hydrophobic nature of the methyl group, and the crystal lattice energies are unusual because acetate is not a spherically symmetric ion that adopts close-packed structures as do the classic inorganic systems (14). Since the methyl group causes a decrease in both the lattice energy and the hydration energy, the question becomes, which is affected more? To make this comparison we can compare, for example, the difference in hydration energy of fluoride and acetate (Table 7) to the difference in lattice energy of sodium fluoride and sodium acetate (Tables 3 and 4). The hydration energy is 123 kJ/mol less exothermic on going from fluoride to acetate, whereas the lattice energy is 165 kJ/mol less endothermic on going from sodium fluoride to sodium acetate. This favors solubility and suggests that the solid-state structures are more affected by the introduction of the acetate ion than the solution structure.

A further complicating factor is the implicit assumption that acetates completely dissociate into the component ions when dissolved in aqueous solution. This is not the case for the transition metal acetates, which often adopt dinuclear structures with bridging acetates, metal-metal bonding, and axial interaction with Lewis bases such as water. Based on the interpretation of their electronic absorption spectra (15), these structures are retained in solution.

Wulfsberg (5, pp 63 and 81) would probably categorize acetate as a feebly basic anion like SO₄²⁻, SeO₄²⁻, and MoO₄²⁻. As he points out, "The solubility of salts of these ions are particularly complex and difficult to predict; ... their tendency to precipitate or not to precipitate varies with the relative magnitudes of the opposing entropy and enthalpy terms." He also notes that "The difficulty in prediction arises from the fact that these anions are just basic enough to have $-T\Delta S$ terms moderately favoring precipitation, with acidic cations; but these anions are so much larger than most acidic cations that the ΔH term is usually unfavorable."

So there you have it. Acetate is one confused little ion, in this author's opinion. Like most compounds containing second period elements (e.g. fluoride), it is unusual. Acetate is an ion that has solubility properties like those of chloride, nitrate, or perchlorate, but is a considerably stronger base than fluoride. It should be noted that a methyl group is a σ -electron donor, and acetate is a stronger base than other similar ions such as formate or nitrite (Table 7). The hydration enthalpies of formate and nitrite are slightly more negative than that of

acetate, consistent with the removal of the hydrophobic methyl group. Furthermore, the relative basicities of formate and nitrite are consistent with the reduced electronegativity of carbon as compared with nitrogen. This is also consistent with Streitwieser's arguments concerning the relative importance of inductive and resonance effects as the dominant factors influencing the acid–base chemistry of carboxylates (16).

Now I feel a little more comfortable modifying my lecture notes and adding “all (or most) acetates are soluble” to the solubility rules discussed in an introductory-level course. I also plan to present a much more detailed discussion of the thermodynamic aspects of solubility the next time I teach advanced inorganic chemistry.

Acknowledgments

I would like to thank Owen Faut and the undergraduates who participated in our discussions, David DeCicco, Jeff Ward, Sara Zuchowski, and any others that I may have forgotten.

Notes

1. It should be noted that the sum of eqs 5 and 6 results in an overall reaction, after canceling gas-phase species, equivalent to the dissolution of an ionic solid. Therefore, the sum of the enthalpies is the heat of solution. Changing the sign then gives the heat of precipitation.

2. Or an undergraduate who has taken an intermediate level inorganic course.

3. At the 95% confidence level. In fact the data calculated from the lead(II) acetate could be rejected on the basis of the *Q* test, to give a mean value of -374 ± 3 kJ/mol at the 95% confidence level.

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- See *Handbook of Chemistry and Physics*, 59th ed.; Weast, R. C., Ed.; CRC: Cleveland, OH, 1978; section “Physical Constants of Inorganic Compounds”. *Soluble* is arbitrarily defined as a solubility greater than or equal to one gram of compound per 100 mL of water.
- (a) K_{sp} data are from Harris, D. C. *Quantitative Chemical Analysis*, 4th ed.; Freeman: New York, 1995. (b) Thermodynamic data are from *Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; CRC: Cleveland, OH, 1990; section 12, pp 1–3. (c) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halo, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *The NBS Tables of Chemical Thermodynamic Properties*; American Chemical Society/American Institute of Physics: Washington, DC, 1982.
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- We actually should be considering lattice enthalpies, since lattice energies are really the free energy associated with the formation of one mole of an ionic solid from its constituent gaseous ions, but the differences between lattice energies and lattice enthalpies are negligible. See G. Rayner-Canham, G. *Descriptive Inorganic Chemistry*; Freeman: New York, 1996; p 91.
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