



Annotating Reaction Equations

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We teachers of general chemistry can be of service to our high school or college students by urging them to annotate the chemical reactions in aqueous solution that they see in their textbooks and that they write in their class notes. An after-the-fact assignment of aqueous-solution reactions into a few recurring categories can help to make our students comfortable with the "goings on" that they observe in their test tubes and read about in their books. Reactions begin to look reasonable and familiar.

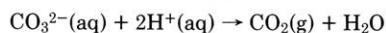
Annotating aqueous solution reactions fosters recognition of the fundamental reaction categories. Ready recognition of a reaction type is the first step toward understanding the "whys and wherefores" inherent in the reaction.

The best understanding of why a chemical reaction proceeds, under constant temperature and pressure conditions, is probably the thermodynamic one, $\Delta G < 0$. Indeed, for chemical reactions in the dry way an analysis of the factors influencing the signs of ΔH and ΔS for a given reaction can be quite rewarding.¹ That sort of analysis, however, is not available for reactions in aqueous solution. The difficulty lies in the role of the solvent in the reaction. The effect of interactions with the solvent on ΔG for the reaction is not visible in the stoichiometric reaction equation.

Since we cannot show our students in detail (i.e., in terms of ΔH and ΔS) how the thermodynamic machinery works for isothermal reactions in aqueous solution, the best we can do for them is to identify certain driving forces or "pusher principles" that usually tend to push a reaction in the direction of the reaction arrow. Once we agree on a catalog of driving forces, we can adopt a code designation for each of them and can use that set of designations for annotating aqueous solution reaction equations.

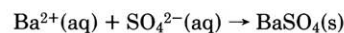
Just as program notes help us to appreciate dramatic or musical performances and as annotations to the moves in a chess game help us to see the significance of those moves, so our driving-force code designations allow us to write program notes or annotations for reactions in aqueous solution.

Gas Formation: GF



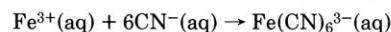
In a GF reaction, the escape of a gaseous product from the solution is the prime driving force (or one of the driving forces) pushing the reaction left to right. Students have no trouble identifying a GF reaction. The gaseous product is clearly marked by a "g" in parentheses or by an upward pointing arrow \uparrow .

Precipitate Formation: PF



In a PF reaction, the formation of an insoluble precipitate is the prime driving force (or one of the driving forces) pushing the reaction left to right. Students have no trouble identifying a PF reaction. The precipitate is clearly marked by an "s" in parentheses or by a downward pointing arrow \downarrow .

Complex Formation: CF



In a CF reaction, the formation of a stable complex is the prime driving force (or one of the driving forces) pushing the reaction left to right.

Beginning students have trouble recognizing complexes. They plaintively ask for an all-encompassing definition. As teachers, many of us prefer to proceed inductively. We show examples of a dozen or so complexes and expect the students to get the idea. Perhaps we should give our students an approximate, general chemistry, definition of a complex like the following.

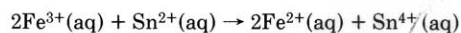
In the common sorts of complexes, a hub metal atom is covalently bound to (shares electrons with) a set of surrounding ligands (a set of surrounding molecules and/or ions). If there are any neutral molecules bonded to the hub atom, the overall configuration is a complex $[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{Ni}(\text{CO})_4]$, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$, etc.]. If there are only anions bonded to the hub atom and the total number of units of negative charge carried by the ligands is less than or greater than the oxidation number of the hub metal atom, the overall configuration is a complex $[\text{FeF}_6]^{3-}$, $[\text{FeSCN}]^{2+}$, $[\text{HgCl}_4]^{2-}$, $[\text{SnCl}_6]^{2-}$, etc.].

In short, a (common) complex involves a metal atom bonded to neutral molecules and/or negative ions; in the case of all the ligands being anions, the resulting combination bears a net electric charge.

When a metal atom and a set of anions form a no net charge combination, we merely refer to the combination (less selectively) as a compound or molecule rather than a complex: CuCN is just a compound, but $[\text{Cu}(\text{CN})_2]^-$ is a complex; SnCl_2 is just a compound, but $[\text{SnCl}_4]^{2-}$ is a complex; $[\text{FeSCN}]^{2+}$ (there are probably aqua ligands as well) is a complex, but $[\text{Fe}(\text{SCN})_3]$ is just a compound; and so on.

(In this "general chemistry" definition of a complex, I have neglected mention of polynuclear complexes and of cationic ligands.)

Redox Interaction: RDX

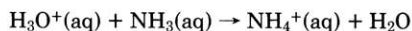


In an RDX reaction, the transfer of electrons from a reducing agent to an oxidizing agent is the prime driving force (or one of the driving forces) pushing the reaction left to right. If, upon checking the oxidation numbers of the ele-

¹ Tykodi, R. J. *J. Chem. Educ.* **1986**, *63*, 107.

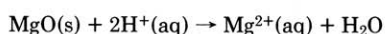
ments appearing in a reaction equation, students see a change for any element, they immediately know that they are dealing with an RDX reaction.

Acid-Base Interaction: ABI



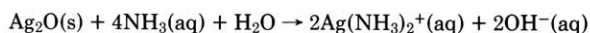
In an ABI reaction, the transfer of protons (H^+) from acid species to base species is the prime driving force (or one of the driving forces) pushing the reaction left to right. If students learn to look for the transfer of a proton in acid-base reactions, they should be quite successful in spotting ABI reactions.

To keep the ABI category within bounds, however, it is useful to distinguish between primary and secondary acid-base interactions. In a primary acid-base interaction the transfer of protons takes place by itself (i.e., without the necessary help of another kind of process) and represents one of the principal driving forces for the reaction. Magnesium oxide, MgO , for example, is essentially insoluble in plain water at room temperature but dissolves in dilute aqueous acid.



The $\text{H}^+(\text{aq})$ ions (ultimately) combine with the oxide ions to form H_2O molecules and thus free the Mg^{2+} ions so that they may go into solution. The proton-transfer process happens by itself.

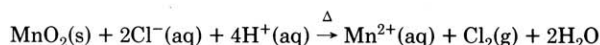
In a secondary acid-base interaction, the proton-transfer process does not take place by itself but requires the help of another principal driving force to induce the reaction. Silver oxide, Ag_2O , for example, is not appreciably soluble in plain water or in dilute sodium hydroxide at room temperature, yet Ag_2O does dissolve in concentrated aqueous ammonia:



The NH_3 molecules complex the Ag^+ ions and thus free the oxide ions so that they can interact with water molecules. The CF process thus induces the secondary acid-base interaction



Again: MnO_2 is not soluble in plain hot water or in hot dilute sulfuric acid, yet MnO_2 dissolves in hot dilute aqueous hydrochloric acid:



The oxidation-reduction process (RDX process) frees the oxide ions and induces the secondary acid-base interaction



Of the acid-base interactions that frequently accompany oxidation-reduction reactions, the majority are secondary acid-base interactions.

Let us use the code designation ABI for primary acid-base interactions and the code designation (ABI) for secondary acid-base interactions. I prefer to neglect secondary acid-base interactions because such interactions do not function as a principal driving force for reactions (reactions 4, 8, 9, 11, 16, 18, 21, 22, and 30 below all show secondary acid-base interactions).

Among the residual or other types of reactions in aqueous solution, there is one that occurs often enough to be worth coding.

Hub-Attack Interaction: HBA



In an HBA reaction (solvolysis, hydrolysis), solvent mole-

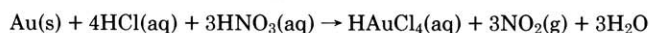
cules "attack" a hub atom (Z) that is bonded to atoms (X) other than oxygen and, in effect, replace some or all of the $\text{Z} \cdots \text{X}$ interactions around the hub atom by $\text{Z} \cdots \text{O}$ interactions; the increased strength of the $\text{Z} \cdots \text{O}$ interaction, relative to the $\text{Z} \cdots \text{X}$ interaction, is the prime driving force (or one of the driving forces) pushing the reaction left to right.

The most common pattern for the HBA reaction is the replacement of covalently bound satellite halogen atoms around a hub atom by oxygen atoms. If students will watch for the "halogen to oxygen" switch, they should readily recognize an HBA reaction.

The three processes precipitation, gas evolution, and complex formation are ways of removing chemical substances from an aqueous environment. The disappearance of the key actors from the aqueous stage is the driving force for the reaction in the direction of the reaction arrow. When the first set of actors disappears, their understudies hop on stage, then disappear, too. The under-understudies hop on stage and go the way of their predecessors. Ultimately the entire drama company disappears. In the case of complex formation, "disappearance" means a change of identity. The actors go into disguise.

ABI and RDX processes involve a tug-of-war as the species compete for protons or electrons. The HBA process has to do with the relative stabilities of $\text{Z} \cdots \text{X}$ and $\text{Z} \cdots \text{O}$ interactions in the aqueous environment.

Sometimes two or more driving forces are simultaneously active in a given reaction. Gold will not dissolve in $\text{HCl}(\text{aq})$ or in $\text{HNO}_3(\text{aq})$ separately but will dissolve in a combination of the two (aqua regia).



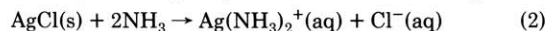
CF, RDX, GF. It seems to take a combination of oxidizing action and complexing action to get gold into solution. Chlorine water is also both oxidizing and complexing, converting gold to soluble chlorohydroxoaurate(III) complexes— AuCl_4^- , AuCl_3OH^- , etc.

Examples

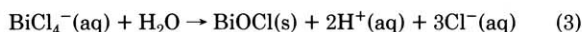
Let us annotate the following reaction equations to see how the system works.



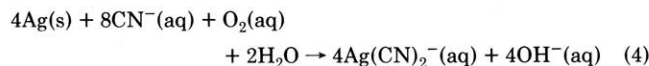
ABI, GF. The acid-base interaction converts SO_3^{2-} to the unstable H_2SO_3 , which decomposes: $\text{SO}_3^{2-} + \text{H}_3\text{O}^+ \rightarrow \text{HSO}_3^- + \text{H}_2\text{O}$, $\text{HSO}_3^- + \text{H}_3\text{O}^+ \rightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$, $\text{H}_2\text{SO}_3 \rightarrow \text{SO}_2 + \text{H}_2\text{O}$. The escape of SO_2 from the solution helps to push the reaction left to right.



CF. The formation of the stable complex $\text{Ag}(\text{NH}_3)_2^+$ pushes the reaction left to right.



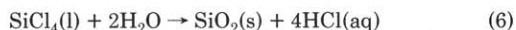
HBA, PF. Diluting the complex BiCl_4^- with water reduces its stability to the point where the insoluble chloride oxide, BiOCl , precipitates from the solution.



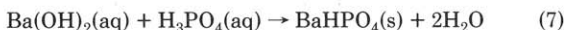
RDX, CF. Silver ores are processed with aqueous CN^- : the redox action of the dissolved oxygen and the complexing action of the CN^- bring the elemental silver (and also compounds of silver such as Ag_2S) into solution; the resulting solution is then treated with zinc to recover the silver: $\text{Zn} + 2\text{Ag}(\text{CN})_2^- \rightarrow 2\text{Ag} + \text{Zn}(\text{CN})_4^{2-}$.



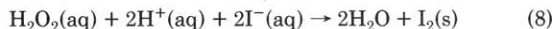
ABI, PF. This sort of gas-forming reaction is used on an industrial scale to prepare from their salts those acids (HF , HCl , HNO_3 , etc.) that are more volatile than (and stable in) H_2SO_4 .



HBA, PF. The greater stability of the Si-O bond relative to the Si-Cl bond and the insolubility of silica, SiO_2 , are responsible for pushing the reaction left to right.



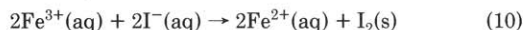
ABI, PF. As a result of the acid-base interaction, protons from H_3PO_4 and hydroxide ions from $\text{Ba}(\text{OH})_2$ ultimately combine to form water; the residual Ba^{2+} and HPO_4^{2-} ions then form the insoluble BaHPO_4 .



RDX, PF. Iodine is not very soluble in water (0.029 g/100 g H_2O at 20 °C), so if we want the iodine produced in the reaction to stay in solution we use an excess of I^- . The liberated I_2 then forms a stable, soluble complex with the excess I^- : $\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-$.



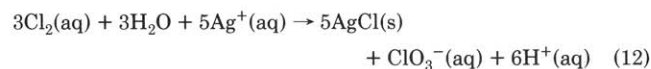
CF.



RDX, PF. See the comment to reaction 8.



RDX, GF, PF. This redox reaction is an example of a disproportionation reaction. An element in an intermediate oxidation state is simultaneously oxidized and reduced. In the present case one sulfur atom is oxidized and the other is reduced.



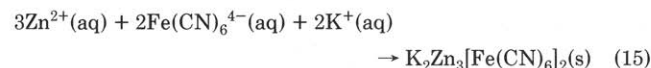
RDX, PF. This redox reaction is a clearer case of a disproportionation process: $\text{Cl}^0 \rightarrow \text{Cl}^{-1}$ and simultaneously $\text{Cl}^0 \rightarrow \text{Cl}^{\text{V}}$.



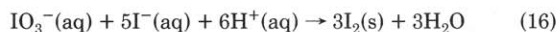
ABI, PF. There is an acid-base interaction between ammonia and water, $\text{NH}_3 + \text{H}_2\text{O} = \text{NH}_4^+ + \text{OH}^-$, producing OH^- ions that bring about precipitation of a gelatinous precipitate of "iron(III) hydroxide". (The precipitate is probably better described as "hydrated iron(III) oxide," $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$).



PF.



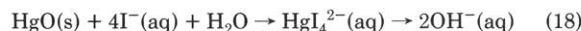
PF.



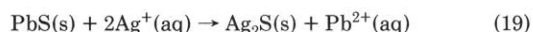
RDX, PF. See the comment to reaction 8. This reaction could be called an "inverse disproportionation reaction" since a higher and a lower oxidation state of an element interact to produce an intermediate state: $\text{I}^{\text{V}} \rightarrow \text{I}^0$, $\text{I}^{-1} \rightarrow \text{I}^0$.



ABI, GF.



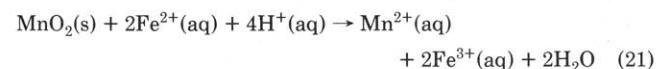
CF.



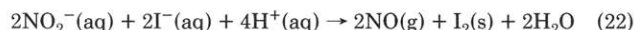
PF. This reaction (a "precipitate exchange" reaction) works because the solubility of Ag_2S in water at room temperature is much less than that of PbS .



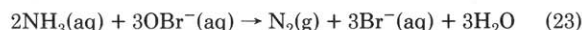
RDX, GF.



RDX.



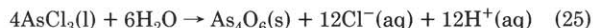
RDX, GF, PF. See the comment to reaction 8.



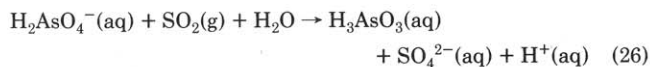
RDX, GF.



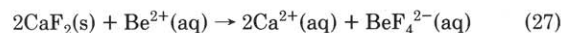
ABI, PF.



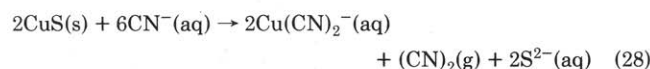
HBA, PF.



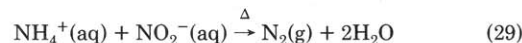
RDX.



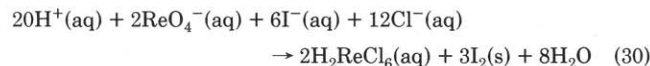
CF.



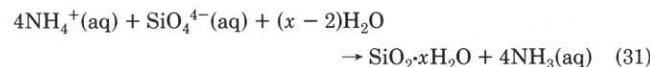
CF, GF, RDX.



RDX, GF.



RDX, CF, PF. See the comment to reaction 8.



ABI, PF.

My recommendations for progressing through a year-course in general chemistry are as follows:

(1) Early in the course introduce the idea of the driving forces (pusher principles) for reactions in aqueous solution. Have the students routinely annotate reactions of type GF, PF, CF, and HBA.

(2) Give a qualitative introduction to acid-base neutralization reactions and to simple redox reactions fairly early in the course. Extend the scheme of annotations to include ABI and RDX reactions.

From this point on, require the routine annotation of aqueous solution reaction equations to foster recognition of the fundamental aqueous solution reaction categories. It is amazing how often students look at reaction equations and fail to recognize the presence of oxidation-reduction or complex formation. Students who have developed the habit of annotating reaction equations are less likely to overlook important features of reactions.

(3) After students have been annotating reactions for some time, discuss with them the circumstances under which they are apt to meet a particular reaction category:

(a) GF: Gases tend to appear in certain redox reactions (H_2 , O_2 , Cl_2 , etc.), in reactions volatilizing certain acids or bases (HF , HCl , H_2S , NH_3 , etc.), and in reactions where unstable acids (H_2CO_3 , H_2SO_3 , $\text{H}_2\text{S}_2\text{O}_3$, etc.) decompose.

(b) PF: Give the students a set of solubility rules describing the solubility characteristics of common inorganic salts: "all nitrates are soluble; all sulfides are insoluble, except for those of . . . ; etc".

(c) CF: Complex formation is an especially important part of the chemistry of the transition metals. Point out the existence of aqua complexes and comment on the differences in behavior of solutions of $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$, and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ relative to $\text{AgNO}_3(\text{aq})$.

(d) RDX: Talk about oxidation numbers and the periodic table. The elements participating in RDX reactions must be of

variable oxidation state. Where in the periodic table do we find such elements?

(e) ABI: Metal oxides (with low oxidation numbers) tend to be base-forming; nonmetal oxides tend to be acid-forming. When species related to or derived from the two kinds of oxides share the same solution environment, there is apt to be an acid-base interaction. (The binary hydrides of Groups 16 and 17 also behave as acids in water.)

(f) HBA: Some of the nonmetal halides of the elements in Groups 14, 15, and 16 hydrolyze in water in the hub-attack fashion.

(4) In the latter part of the course, when aqueous equilibria are treated quantitatively via solubility product constants, stability constants for complexes, acid and base ionization constants, and standard electrode potentials, point out that the strength of the corresponding pusher principle is related to the numerical value of the relevant equilibrium constant.

(5) Finally, after having developed thermodynamic ideas to the point of being able to refer to ΔG , ΔH , and ΔS for chemical reactions, explain to the students that the catalog of driving forces or pusher principles is simply a catalog of circumstances that are usu-

ally correlated with a decrease in Gibbs free energy for the reaction ($\Delta G < 0$).

Where possible, show how a particular reaction category is "explained" thermodynamically. A GF process, for example, usually leads to a favorable sign of ΔS for the reaction (favorable for left-to-right reaction).

By carrying our students through the suggested levels of appreciation for chemical reactions in aqueous solution—annotation (all year long), discussion of circumstances, quantitation, thermodynamic correlation and "explanation"—we should be more likely (than is now the case) to turn out students who are chemically literate. It is almost inconceivable that a student who spent a year annotating hundreds of chemical reaction equations (aqueous solutions) and who related PF reactions to a set of solubility rules would be tempted to describe silver chloride as a "pale green gas".²

² Davenport, D. A. *J. Chem. Educ.* **1970**, *47*, 271.