STRENGTHENING CONCEPTUAL CONNECTIONS

IN INTRODUCTORY CHEMISTRY COURSES

by

George M. Bodner

Department of Chemistry

Purdue University

West Lafayette, IN 47907

gmbodner@purdue.edu

Phone: (765) 494-5313

FAX: (765) 494-0239

ABSTRACT

Both research on learning across a wide range of disciplines and common theories of learning recognize the importance of learning through making connections between new concepts to which one is exposed and existing cognitive structures or schema. This paper considers examples of underappreciated cognitive connections that our experience has shown can facilitate students' learning of chemistry in the introductory course. The first deals with the question of whether the "common-ion effect" is limited to discussions of solubility product equilibrium, as many textbooks seem to indicate. The second example questions why certain traditional approaches to teaching the chemistry of conjugate oxidizing agents and reducing agents are not applied to discussions of the chemistry of conjugate Brønsted acids and bases.

INTRODUCTION

When I entered the field of chemical education, one of the dominant perspectives was that of Piaget (Herron, 1975: Herron, 1978; Good, Mellon & Kronhout, 1978), which focused on stages of intellectual development and questioned whether it was possible for students to learn certain ideas or concepts until they had reached an appropriate level of epistemic development. In recent years, there has been a growing appreciation of the view of learning proposed by Vygotsky (1986) and others, which focuses on learning through interactions with different people, objects, events, experiences, and contexts. Both of these perspectives on learning are consistent with theoretical models proposed by Ausubel (1978) and Gagné and White (1978) that emphasize the importance of learning through making connections between new concepts to which one is exposed and existing cognitive

structures or schema.

The importance of cognitive connections in learning has been invoked across a wide range of disciplines, from art (Korosckik, 1996) to physics (Robertson, 1990). Major and Palmer (2001) argued that cognitive connections play an important role in problem-based learning and Mastropieri and Scruggs (1996) have argued that the failure to make cognitive connections between already known and to-be-learned information that was a primary characteristic of students referred to special education. Cross (1999) has gone so far as to assert that "Learning is about making connections."

This paper considers examples of seldom-appreciated connections that I have found can facilitate students' learning of chemistry. One of these examples questions the conventional wisdom that the common-ion effect is limited to solubility product equilibria. The other revolves around the question: Considering the ubiquitous presence of tables of redox half-reactions in introductory chemistry textbooks, why don't analogous tables appear in discussions of Brønsted acids and bases? As evidence for the power of these tables, the reader might consider the following question before continuing with this paper: Would you expect the following acid-base reaction to proceed as written? I.e., would you expect the overall equilibrium constant for this reaction to be larger than 1?

$$HSO_4^-(aq) + H_2PO_4^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H_3PO_4(aq)$$
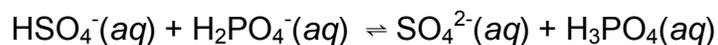
The Common-Ion Effect

The shelves that line one wall of my office complex contain more than 200 introductory general chemistry textbooks, enough books to fill more than 9 m of shelf space. It doesn't matter which book one pulls from the shelf, the index at the back contains

an entry on the "common-ion effect." As might be expected, many of these texts use the same example, the decrease in the solubility of AgCl in a solution that contains either the Ag^+ or Cl^- ion.

$$AgCl(s) \overset{H_2O}{\rightleftharpoons} Ag^+(aq) + Cl^-(aq)$$

$$NaCl(s) \overset{H_2O}{\rightarrow} Na^+(aq) + Cl^-(aq)$$
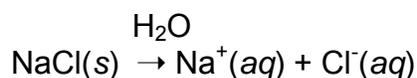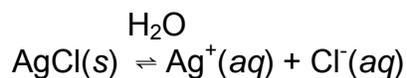
Perhaps it is not surprising to find the common-ion effect defined as the "decrease in solubility of an ionic salt, i.e., one that dissociates in solution into its ions, caused by the presence in solution of another solute that contains one of the same ions as the salt" (Lagasse, et al., 2000).

If one agrees with Ausubel (1978) that "The most important thing influencing learning is what the learner already knows," it is somewhat disconcerting to note that relatively few introductory texts note that a "common-ion effect" also occurs in buffer solutions. Consider a traditional 0.10 M CH_3CO_2H/0.10 M CH_3CO_2Na buffer, for example.

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

$$CH_3CO_2Na(aq) \overset{H_2O}{\rightleftharpoons} Na^+(aq) + CH_3CO_2^-(aq)$$
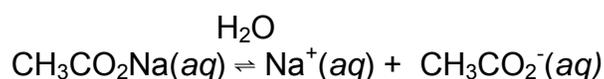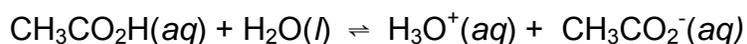
Many, if not most, instructors invoke LeChátelier's principle to explain why the addition of sodium acetate raises the pH of the solution by decreasing the extent to which acetic acid dissociates. But it is rare to find either instructors or textbooks that explicitly make the connection between the "common-ion effect" in this buffer and the "common-ion effect" in their discussion of the solubility of silver chloride. It is interesting to note that one of the places where this connection is made is the Wikipedia (2006), which uses the example of

an acetic acid/sodium acetate buffer solution to introduce the idea of the common-ion effect.

I have no objection to invoking LeChátelier's principle in discussions of buffer solutions. If one believes the concept of a "common-ion effect" is important for students to learn, however, this might be better achieved by noting that it is the presence of a common ion that inhibits both the dissociation of a weak acid in a buffer solution and the dissociation of an "insoluble" salt in a solution that contains a source of a common ion.

Indeed, if one accepts the notion that making connections between analogous situations can facilitate learning, one might conclude that the buffer example cited above is not the only example of a "common-ion effect" one might invoke. Consider one of the first examples students encounter when they are exposed to discussions of equilibria — aqueous solutions of weak acids such as acetic acid.

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

$$2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$
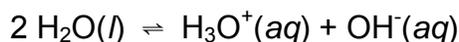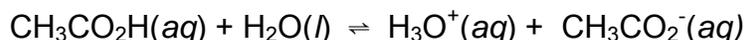
The total concentration of the H_3O^+ ion in an 0.10 M CH_3CO_2H solution from the dissociation of both the weak acid and water is presumed to be 0.0013 M. The contribution to the total concentration of the H_3O^+ ion from the dissociation of water, however, must be equal to the concentration of the OH^- ion from the dissociation of water. If the pH of this solution is 2.9, this means that the contribution to the concentration of the H_3O^+ and OH^- ions from the dissociation of water has been decreased by four orders of magnitude.

0.10 M CH_3CO_2H (pH 2.9): $\left[H_3O^+ \right]_w = \left[OH^- \right]_w = 7.7 \times 10^{-12}\ M$

This is an obvious example of LeChátelier's principle, but it also another example of a

"common-ion effect." The addition of a second source of the H_3O^+ ion leads to a

significant decrease in concentration of this ion from the original source of this ion.

TABLES OF OXIDATION-REDUCTION HALF REACTIONS

It is difficult to trace the history of the use of tables of electromotive force back to

determine the date at which they first appeared in chemistry textbooks. A table of the

"electromotive series" can be found, however, as early as 1913, in W. A. Noyes's *A*

Textbook of Chemistry (Noyes, 1913). According to a footnote in Noyes's text, this table

was based on data reported by Wilh. Palmaer in Nernst's Festschrift in 1907.

By 1925, tables of electromotive force had sufficient explanatory and predictive

power in the minds of textbook authors that Deming (1925) began his chapter on

electrochemistry as follows: "The electrochemical series, in its simplest form, is a list of

oxidizable substances (metals). Read from below upward, it gives the order of

increasing ease of oxidation. Metals nearest the top are the most readily oxidized, that

is they part most readily with electrons to form cations ..." Deming then presented a

table written in the form of oxidation half-reactions accompanied by the corresponding

half-cell potentials in volts.

Oxidizable substances (Reducing agents)		Reducible substances (Oxidizing agents)	Potential (In volts)
Li	$\rightleftharpoons$	$Li^+ + e^-$	+2.96
K	$\rightleftharpoons$	$K^+ + e^-$	+2.92
Na	$\rightleftharpoons$	$Na^+ + e^-$	+2.72
Mg	$\rightleftharpoons$	$Mg^{++} + 2e^-$	+1.55

Al	$\rightleftharpoons$	$Al^{+++} + 3e^-$	+1.35
Zn	$\rightleftharpoons$	$Zn^{++} + 2e^-$	+0.75
Fe	$\rightleftharpoons$	$Fe^{++} + 2e^-$	+0.45
Cd	$\rightleftharpoons$	$Cd^{++} + 2e^-$	+0.40
Ni	$\rightleftharpoons$	$Ni^{++} + 2e^-$	+0.21
$\vdots$		$\vdots$	$\vdots$

On each side of this table, Deming placed a label with an arrow pointing up that was accompanied by the caption: "Order of increasing ease of oxidation or increasing activity as reducing agents."

By 1944, introductory chemistry textbooks often linked reducing agents with oxidizing agents in tables that showed the relative strengths of the reducing agents as proceeding from "strong" to "weak" as one went down the column of half-reactions, while the corresponding oxidizing agents went from "weak" to "strong" (Timm, 1944). Tables of the electrochemical series had sufficient explanatory power that many chemistry classrooms once had a table of oxidation half-cell potentials prominently posted on one of the walls of the room. With time, the convention for half-cell potentials was changed, so that these tables eventually appeared as lists of reduction half-cell reactions.

The first edition of the textbook by Nebergall and Schmidt (1957), which eventually went through ten editions and sold more than a million of copies, noted that the electromotive series of the elements helps us: (1) identify metals that are most

easily oxidized and are therefore good reducing agents; (2) identify metal ions and nonmetals in their elemental states that are good oxidizing agents; and (3) predict which redox reactions should occur.

It is only recently that discussions of the electrochemical series have made explicit use of the term *conjugate* to link a given oxidizing agent to the corresponding reducing agent in a given half-reaction. Thus, whereas the notion that the relative strength of a given reducing agent is linked or coupled to the relative strength of the corresponding oxidizing agent has long been a feature of introductory chemistry textbooks, it is only in the last few decades that one finds explicit mention of the fact that strong reducing agents (such as Na) have weak conjugate oxidizing agents (such as the Na^+ ion), whereas strong oxidizing agents (such as F_2) are linked by the reduction half-reaction to a weak conjugate reducing agent (such as the F^- ion).[1]

BRØNSTED ACID-BASE REACTIONS

The ubiquitous presence of tables of redox half-reactions in introductory chemistry textbooks raises an interesting question: Why don't analogous tables routinely appear in discussions of Brønsted acids and bases? The philosophical and conceptual basis of the phenomena are similar.

- Both systems can be described in terms of coupled or linked pairs of reagents, i.e., conjugate pairs.

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[1] I have noticed that it is the rare individual, indeed, who enters one of his chemistry courses who has not been asked "to conjugate" a verb. I therefore finds it interesting to note that it is even rarer to find anyone in these courses who has been told by one of their language teachers that "to conjugate" means "to link or couple."

$$\text{acid} \ + \ \text{base} \ \rightleftharpoons \ \text{conjugate base} + \text{conjugate acid}$$

$$\text{OA} \ + \ \text{RA} \ \rightleftharpoons \ \text{conjugate RA} + \text{conjugate OA}$$
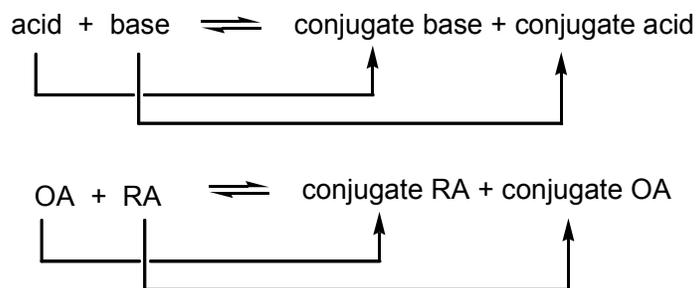
- Both systems involve the transfer of a particle. In one case, the transfer of a proton.

$$HSO_4^-(aq) + H_2PO_4^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H_3PO_4(aq)$$
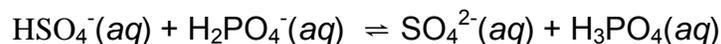
In the other case, the transfer of one or more electrons,

$$2\,Ag^+(aq) + Cu(s) \rightleftharpoons 2\,Ag(s) + Cu^{2+}(aq)$$
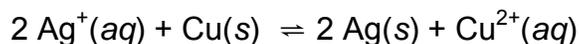
or one or more atoms.

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$
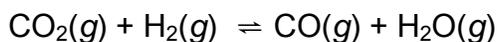
- In both systems there is a relationship between the relative strengths of the two components of the half-reaction; a strong oxidizing agent is linked to a weak reducing agent, a strong acid is linked to a weak conjugate base.

- In both systems, one can predict whether a reaction should occur by asking: On which side of the equation do the stronger agents appear? The stronger of a pair of reducing agents and the stronger of a pair of oxidizing agents should react to form the weaker reducing agent and the weaker oxidizing agent.

$$2\ Ag^+(aq)\ +\ Cu(s)\ \rightleftharpoons\ 2\ Ag(s)\ +\ Cu^{2+}(aq)$$

stronger   stronger   weaker   weaker
oxidizing   reducing   reducing   oxidizing
agent   agent   agent   agent
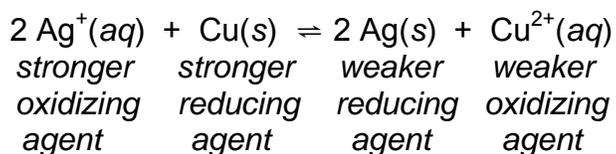
In a similar manner, the stronger of a pair of Brønsted acids and the stronger of a pair of Brønsted bases should react to form the weaker Brønsted acid and the weaker Brønsted base.

$$HSO_4^-(aq) + H_2PO_4^-(aq)\ \rightleftharpoons\ SO_4^{2-}(aq) + H_3PO_4(aq)$$

stronger   stronger   weaker   weaker
acid   base   base   acid
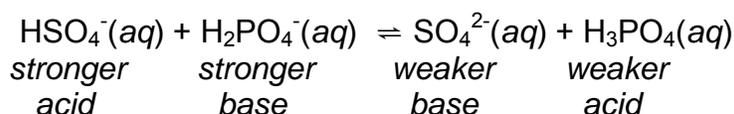
Thus, in theory, a table of Brønsted acid-base reactions has the potential to serve functions that are analogous to those filled by tables of redox half-reactions. Paraphrasing the words of Nebergall and Schmidt (1957), such a table can help us: (1) identify substances that lose a proton with relative ease, which are therefore good acids; (2) identify compounds that have a relatively high affinity for a proton and are therefore good bases; and (3) predict acid-base reactions that should occur.

CONCLUSION

For some time, I have had considerable success convincing the students in both my introductory chemistry courses and the physical chemistry course I teach for students from the life sciences of the benefit of recognizing an explicit connection between the concepts of conjugate acid/base pairs and conjugate oxidizing/reducing agent pairs. In the absence of a controlled experiment, or even a quasi-experimental design, I merely report an increase in the percentage of students who seem to be able to handle questions such as the following, which was answered correctly by 95% of the students on a recent introductory chemistry exam.

$NaHCO_3$ can be used to neutralize strong bases, such as $NaOH$. What conclusion can be drawn from the fact that the following acid-base reaction proceeds to the right as written?

$$HCO_3^-(aq) + OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$$
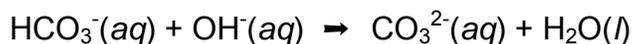
(a) HCO_3^- is a stronger acid than H_2O

(b) HCO_3^- is a stronger base than CO_3^{2-}

(c) HCO_3^- is a stronger base than OH^-

(d) CO_3^{2-} is a stronger base than OH^-

(e) H_2O is a stronger acid than HCO_3^-

On the basis of this success, I have added the following table to his most recent textbook (Spencer, Bodner & Rickard, 2005).

Relative Strengths of Typical Brønsted Acids and Bases

	acid	conjugate base	K_a (at 25°C)
Best	$HI \rightleftharpoons H^+ + I^-$		3×10^9
Brønsted	$HClO_4 \rightleftharpoons H^+ + ClO_4^-$		1×10^8
Acids	$HCl \rightleftharpoons H^+ + Cl^-$		1×10^6
	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$		1×10^3
	$HClO_3 \rightleftharpoons H^+ + ClO_3^-$		5×10^2
	$H_3O^+ \rightleftharpoons H^+ + H_2O$		55
	$HNO_3 \rightleftharpoons H^+ + NO_3^-$		28
	$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^{2-}$		9.6

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	1.2×10^{-2}
$HClO_2 \rightleftharpoons H^+ + ClO_2^-$	1.1×10^{-2}
$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	7.1×10^{-3}
$HF \rightleftharpoons H^+ + F^-$	7.2×10^{-4}
$CH_3CO_2H \rightleftharpoons H^+ + CH_3CO_2^-$	1.8×10^{-5}
$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	4.5×10^{-7}
$H_2S \rightleftharpoons H^+ + HS^-$	1.0×10^{-7}
$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$	6.3×10^{-8}
$HClO \rightleftharpoons H^+ + ClO^-$	2.9×10^{-8}
$H_3BO_3 \rightleftharpoons H^+ + H_2BO_3^-$	7.3×10^{-10}
$NH_4^+ \rightleftharpoons H^+ + NH_3$	5.8×10^{-10}
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	4.7×10^{-11}
$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$	4.2×10^{-13}
$HS^- \rightleftharpoons H^+ + S^{2-}$	1.3×10^{-13}
$H_2O \rightleftharpoons H^+ + OH^-$	1.8×10^{-16} [2]
$CH_3OH \rightleftharpoons H^+ + CH_3O^-$	1×10^{-18}
$HC{\equiv}CH \rightleftharpoons H^+ + HC{\equiv}C^-$	1×10^{-25}
$NH_3 \rightleftharpoons H^+ + NH_2^-$	1×10^{-33}

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[2]The value of K_a for water is equal to the value of K_w divided by concentration of water in moles per liter at 25°C.

$$H_2 \;\rightleftharpoons\; H^+ + H^-$$ Best 1×10^{-35}

$$CH_2{=}CH_2 \;\rightleftharpoons\; H^+ + CH_2{=}CH^-$$ Brønsted 1×10^{-44}

$$CH_4 \;\rightleftharpoons\; H^+ + CH_3^-$$ Bases 1×10^{-49}

This table summarizes the relative strengths of Brønsted acids and bases by organizing the reactions in which a given acid is converted into its conjugate base such that the strongest Brønsted acids are in the upper-left corner of this table; the strongest Brønsted bases in the bottom-right corner.

This table can be used to predict whether certain acid-base reactions should occur. For example, it predicts that acetylene should react with sodium amide because the NH_2^- ion is a strong enough base to remove a proton from acetylene to form the acetylide ion.

$$HC{\equiv}CH \;+\; NH_2^- \;\rightleftharpoons\; HC{\equiv}C^- \;+\; NH_3$$

stronger *stronger* *weaker* *weaker*
acid *base* *base* *acid*
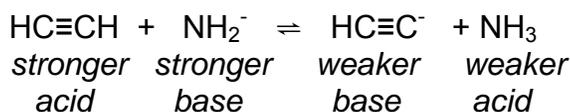
It also predicts that methanol should react with sodium hydride because the H^- ion should be a strong enough base to remove the acidic proton from methanol.

$$CH_3OH \;+\; H^- \;\rightleftharpoons\; CH_3O^- \;+\; H_2$$

stronger *stronger* *weaker* *weaker*
acid *base* *base* *acid*
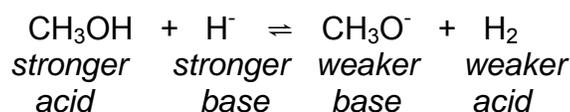
This table therefore provides a basis upon which our colleagues who teach organic chemistry can build their discussions of Brønsted acid-base concepts as they extend this concept to reactions that do not occur in aqueous solution. This is not a problem, however, because electrode potentials have been used in a similar fashion for decades to analyze oxidation-reduction reactions that do not always occur in aqueous solutions.

It should be noted that many contemporary chemistry textbooks contain tables that provide lists of Brønsted acids and their corresponding Brønsted bases (Brown, LeMay and Burstein, 1999; Kotz and Treichel, 2003; Atkins and Jones, 2002), and that virtually all current texts discuss the implications of the existence of conjugate acid/base pairs in the Brønsted theory. What is missing from these textbooks, however, is an explicit connection between discussions of the proton transfer that lies at the heart of Brønsted acid/base reactions and discussions of electron transfer that can occur in oxidation-reduction reactions. What is also missing is a mechanism for quantifying the relative strengths of components of the tables of conjugate acid/base pairs found in many textbooks.

The difference between tables of redox half-reactions and Brønsted acid-base reactions historically has been the ability to quantify the relative strengths of oxidizing and reducing agents by adding cell potentials to the table of half-cell potentials. A similar result can be achieved, however, by adding acid-dissociation equilibrium constants to the table of Brønsted acid-base reactions.

Those who question the use of K_a as a means of quantifying the relative magnitude of Brønsted acids or Brønsted bases might wish to look at Pauling's general chemistry textbook (Pauling, 1970). Next to each half-reaction in his table of redox half–reactions he lists not only the value of the half-cell potential but also the equilibrium constant for that half-reaction that would be extracted from that half-cell potential. The entry in his table for the Na/Na^+ half-reaction, for example, is written as follows.

$$E^{o} \qquad K$$

$$Na \; \rightleftharpoons \; Na^{+} + e^{-} \qquad 2.712 \qquad 4.0 \times 10^{45}$$
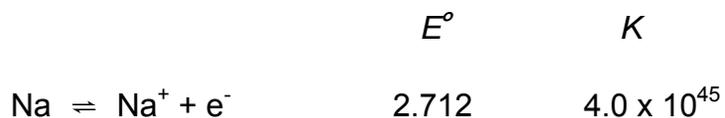
The values of K_a in the proposed table of Brønsted acids and their conjugate bases serves the same function as the value of K in Pauling's table of redox half-reactions.

I have had considerably less experience incorporating the connection between weak acid, buffer solution and solubility product calculations in his introductory and physical chemistry courses. Anecdotal conversations with students in these classes when this connection has been made, however, have lead him to believe that the students understand and appreciate the connection being made. Students in the physical chemistry class also seem to appreciate the difference between this approach and the dogmatic approach certain textbooks take, which would restrict, by definition, application of the term "common-ion effect" to only those situations that involve the solubility of an ionic substance in the presence of another solute.

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