Chapters 18 & 19. Cracolice, 2/e. Chemistry X11.

Chapter 18. Acid-base (proton-transfer) reactions.

⇒ There is a **practice quiz** for Ch 18 at the web site.

This is a major chapter. It usefully builds on the recent chapters on solutions as well as some earlier material. A thorough understanding of Ch 18 will lay a good base for discussing Ch 19 & 20. And the focus topic of this chapter is just plain important.

Ch 18 is on acids and bases, which are of common interest. We discuss various descriptions of acid and bases. (Yes, there's more than "acids give off H^+".) We revisit strong and weak acids (recall Sect 17.3). Be sure to distinguish acid (or base) strength from concentration: strength is a property of the chemical; concentration is a measure of the amount present.

You should know the common strong acids (Sect 17.3). Remember, most acids are weak.

We discuss the ionization of water itself; water gives off the characteristic ions of both acids and bases -- in equal numbers, and is therefore neutral. Sect 18.8, on K_w, introduces the important idea of equilibrium constants; more in Ch 20. Sect 18.9 establishes the concept of pH, a common measure of acidity.

⇒ One common way to indicate the molarity of a solution is to use square brackets. That is, the statement "The concentration of sodium ions is 0.1 mol/L" can be written as "$[Na^+] = 0.1$ M". We mentioned this with Ch 16; Cracolice now formally introduces it, page 513.

⇒ The pH scale is open-ended. There is no maximum or minimum possible pH value. Indeed, most pH values that we encounter are between 0 and 14 (e.g., Cracolice, p 516). However, those are practical limits, not theoretical limits. To say something like "The pH scale runs from 0 to 14" is simply incorrect. Example: Using the textbook formula for pH, the pH of a solution with $[H^+] = 10$ M is -1. Now, there are more complexities with solutions of very strong acids or bases, but this does illustrate that a pH below 0 is possible.

Sect 18.10 introduces no new chemistry at all; it's just a little more math. And the math is simple enough with a scientific calculator. You now need to learn your log and 10^x keys. (Please see me if you need some help with the calculator for this.) Most real pH's are non-integers; I strongly encourage you to do this section.

> When you start dealing with logs, you need a new rule for significant figures. In a logarithm, only the decimal part of the number (the digits to the right of the decimal point) is "significant". The underlying reason for this is that the integer part of a log (before the decimal point) reflects the exponent. Cracolice introduces this well on p 519. This is not an important issue for us at this level; if you want, a good simple habit is to report pH's to two decimal places.

Figs 18.2 & 3 are good focal points. Be sure you understand what is going on in these Figs.

Sect 3 is optional. It discusses one further model to describe acids and bases.

Supplementary worksheets

Four of the self-help worksheet files I have posted on my Chemistry Practice Problems page are relevant to Ch 18. One is on water; it discusses the ionization of water, and introduces pH. The others are on strong acids, weak acids, and buffers. The worksheets provide many practice problems, from basic to difficult, with answers.

Chapter 19. Oxidation-reduction (redox) reactions.

Read Sect 1-7.

Ch 18 is on acids and bases and their reactions; that is, it focuses on reactions involving protons (= H^+ ions). Ch 19 is very analogous, but for redox reactions -- reactions involving electrons. The battery is a common example. The basic ideas of electron transfer (Ch 19) follow straightforwardly if you are comfortable with proton transfer (Ch 18). For example, “Predicting Redox Reactions” (Sect 19.6 and Table 19.2) is entirely analogous to “Predicting Acid-base Reactions” (Sect 18.6 and Table 18.1). The twin Sections 18.7 & 19.7 are an explicit comparison. Recall a brief introduction to redox reactions in Ch 8 (especially Sect 7, 8). Oxidation numbers were briefly introduced in Ch 6, p 142.

> [You can skip Sect 19.8. It covers a method for balancing complex redox equations.]

Don’t be intimidated by the vocabulary in this chapter. Watch the electrons, and make sure they balance. You can add terms (e.g., oxidation = loss of electrons; remember LEO) later, but first follow the phenomenon of electron transfer reactions.

Sect 3. Oxidation numbers (ON) are always assigned per atom. It may be meaningful or even useful to talk about the total of the oxidation numbers in a molecule (zero) or ion, but start with ON per atom. Example: The ON of hydrogen in H_2O is +1 -- per H atom.

As Cracolice notes near the very end of the section, ON are bookkeeping devices, to help us keep track of electrons even in species without obvious charges. They do not always have a simple physical meaning.

Errata

p 539, Example 19.9. The lines in the two sets of parentheses are probably supposed to be arrows (→ and ←, respectively)

Further reading (both Ch)

W de Vos & A Pilot, Acids and bases in layers: The stratal structure of an ancient topic. J Chem Educ 78(4):494, 4/01. Discusses various notions of acids and bases.

R Hoffmann, Hi O Silver. Amer Sci 89:311, 7/01. Nobelist Roald Hoffmann writes delightful essays. This one happens to be about oxidation states. (The title, in one variation or another, is the basis of a Lone Ranger-chemistry joke.)

J N Galloway et al, The nitrogen cascade. BioScience 53:341, 4/03. Nitrogen probably has more common oxidation states than any other element, certainly than any other major element. 80% of air is N(0) (in the form of N_2); N(-3) (in the form of amines, closely related to ammonia) is a major constituent of biological materials; N(+5) (as nitrates) is common in fertilizers. N moves among all those states and more, due to diverse biological and non-biological reactions. Understanding the biogeochemical “nitrogen cycle” is important -- and complex. The article listed here is the first of a series of five articles in this issue, on various aspects of nitrogen in nature, with some emphasis on its role as pollution. There are other articles on the N cycle below.

T Clarke, Music and Chemistry: Organ failure. Nature 427:19, 1/1/04. News feature. Corrosion is a redox problem. And many of the pipe organs of Europe are corroding.

H T Dinh et al, Iron corrosion by novel anaerobic microorganisms. Nature 427:829, 2/26/04. Corrosion is, as a generality, unwanted oxidation. Anaerobic corrosion is typically mediated by bacteria, but the details remain unclear. This article summarizes what is known, and reports some novel bacteria that oxidize metallic iron with sulfate ions. The efficiency of the process suggests that the bacteria are directly transferring electrons from the iron to their electron transport chain. Also see Liu et al (2004), and see Lovley (2006) for a review.

H Liu et al, Production of electricity during wastewater treatment using a single chamber microbial fuel cell. Environ Sci Technol 38:2281-2285, 4/04. It’s possible to set up a system in which bacterial oxidation is linked directly to an electrode. (Recall Dinh et al, 2004.) Here they study the use of such bacteria-based fuel cells to clean up wastewater, and generate a little electricity, too. Also see Lovley (2006) for a review.

R Coontz & B Hanson, Not so simple. Science 305:957, 8/13/04. This is an introductory article to a feature section “Toward a Hydrogen Economy”. The articles cover a wide range of topics; I encourage those interested in either the science or policy aspects of this topic to at least browse this section.

M Juhasz et al, The strongest isolable acid, Angew Chem Int Ed 43:5352-5355, 10/11/04. Our discussion of acid strength focused on aqueous solutions. Generalizing on the concept allows one to recognize even stronger acids than those we discussed. Here they report on a family of acids based on halogenated carbon-boron cage structures, such as $H(CHB_{11}H_5Cl_6)$.

M M M Kuypers et al, Massive nitrogen loss from the Benguela upwelling system through anaerobic ammonium oxidation. PNAS 102:6478, 5/3/05. This paper shows the importance of the recently recognized microbiological process, called anammox (anaerobic ammonia oxidation), which makes N_2 from NH_3: $NH_4^+ + NO_2^- \rightarrow N_2 + H_2O$. See Galloway et al (2003) for a broad view of nitrogen cycles.

J M Headrick et al, Spectral signatures of hydrated proton vibrations in water clusters. Science 308:1765, 6/17/05. "The ease with which the pH of water is measured obscures the fact that there is presently no clear molecular description for the hydrated proton."

N Gruber, Oceanography: A bigger nitrogen fix. Nature 436:786, 8/11/05. News. More about the nitrogen cycle. The process of "fixing" atmospheric N (reducing it from "inert" N_2 to useful NH_3) is a major biological process. The work discussed here demonstrates how important biological nitrogen fixation is in the ocean. See Galloway et al (2003) for a broad view of nitrogen cycles.

M Edmonds & T M Gerlach, The airborne lava-seawater interaction plume at Kilauea Volcano, Hawaii. Earth and Planetary Science Letters 244:83-96, 4/15/06. A study of gases that result when lava meets seawater. Of particular interest is the HCl that results from the boiled seawater. They suggest that the amount of HCl added to the atmosphere is usually moderate at Kilauea, but that it could be very serious with larger lava flows.

D R Lovley, Bug juice: harvesting electricity with microorganisms. Nature Reviews Microbiology 4:497, 7/06. Recall Dinh et al (2004) and Liu et al (2004). Good overview and update. A nice feature is that many items in the reference list are annotated. Also see Computer Resources.

J T Hynes, Physical chemistry: The peripatetic proton. Nature 446:270, 3/15/07. News. Discusses recent work showing how protons are transferred from an acid to a base by sequential proton transfer through water bridges, i.e., through H_3O^+. They do infrared (IR) spectroscopy on a ps (picosecond, 10^{-12} s) time scale.

G V Subbarao et al, Can biological nitrification inhibition (BNI) genes from perennial Leymus racemosus (Triticeae) combat nitrification in wheat farming? Plant Soil 299:55-64, 10/07. Some articles above discuss aspects of the complex biogeochemical nitrogen cycle, which involves multiple oxidation states. (See Galloway et al, 2003, for a broad view of nitrogen cycles.) Here the focus is on nitrification, the oxidation of NH_4^+ to NO_3^-, by soil bacteria, which can lead to a loss of ammonia fertilizer as N_2O. A recent discovery is that some plants make inhibitors of nitrification. In this paper, they show that transfer of a chromosome coding for BNI from a wild wheat to an agricultural wheat leads to BNI production by the latter. In principle, this might be a useful crop improvement, and might replace use of a synthetic nitrification inhibitor that is applied to the fields.

M Armand & J-M Tarascon, Building better batteries. Nature 451:652, 2/7/08. An overview of batteries, including new developments and challenges for the future. Part of a series of "Horizons" articles, intended to give a vision of the future. Also see Smith & Gray (2010).

V J. Fabry, Ocean science: Marine calcifiers in a high-CO_2 ocean. Science 320:1020, 5/23/08. News. Some articles above deal with the nitrogen cycle in the oceans. This one deals with the acidity of the oceans. The key point is that rising levels of atmospheric CO_2 lower the pH of the ocean. This affects the availability of carbonate for marine organisms that make $CaCO_3$

skeletons. Work with a variety of organisms suggests that the effects vary. Although the details of the story can get complex, the basic chemistry is at Intro Chem level; it is also a good biology story.

F A Gallagher et al, Magnetic resonance imaging of pH in vivo using hyperpolarized ^{13}C-labelled bicarbonate. Nature 453:940, 6/12/08. Carbonic acid is a weak acid. The amount of it that is in the form of HCO_3^- (hydrogen carbonate or bicarbonate ion) depends on the pH. NMR study of the C can thus determine the pH. However, the method required technical advances in order to become practical. From the journal summary: “The pH value of tissues in a living organism can vary, and alterations in tissue pH have been implicated in a variety of diseases, including cancer. A non invasive method has now been devised that allows the monitoring of the extracellular pH in living mice. The findings also confirm that the pH in a tumour is lower that the one of normal tissue and it is hoped that this technique can be exploited in humans to diagnose and monitor disease processes.”

T S Zwier, Squeezing the water out of HCl(aq). Science 324:1522, 6/19/09. News. “The controlled formation of clusters confined to helium droplets shows that just four water molecules are sufficient to dissolve hydrochloric acid into its ions.” Besides the curiosity aspect, the work on such micro-droplets is relevant to atmospheric and interstellar chemistry.

M Voss & J P Montoya, Nitrogen cycle: Oceans apart. Nature 461:49, 9/3/09. News. A short overview of some recent developments in our -- still quite incomplete -- understanding of the nitrogen cycle. “Reactive nitrogen is lost from the oceans as dinitrogen -- N_2 -- produced by microbial metabolism. The latest twist in an ongoing story is that different pathways dominate in two of the oceanic regions concerned.” (See Galloway et al, 2003, for a broad view of nitrogen cycles.)

Donald J Wuebbles, Nitrous oxide: No laughing matter. Science 326:56, 10/2/09. News. This short news item is an overview of atmospheric nitrous oxide, N_2O. N_2O destroys ozone, and is a greenhouse gas. It is both made and used by natural biological systems, and is affected by human activities. The global budget of N_2O is not completely characterized. The main message here is that N_2O deserves more attention. (See Galloway et al, 2003, for a broad view of nitrogen cycles.)

M J Smith & F M Gray, Batteries, from cradle to grave. J Chem Educ 87:162, 2/10. An overview of current batteries, with an emphasis on environmental issues, including recycling. The article includes a nice table of battery types. Also see Armand & Tarascon (2008).

D F Jarosz & S Lindquist, Hsp90 and environmental stress transform the adaptive value of natural genetic variation. Science 330:1820, 12/24/10. “A molecular chaperone both buffers and potentiates the adaptive nature of genetic variation in yeast.” “Buffers” resist change. A common context in chemistry is acid-base buffers, solutions that resist changing the pH when acids or bases are added. Cracolice discusses these a bit in Ch 20 (p 576). However, the term can be used in other contexts. This paper discusses the idea that certain proteins that can hold onto and help fold incorrectly folded proteins may play a role of buffering genetic variation. (These proteins are known as chaperones, or heat shock proteins.)

B Scaillet & F Gaillard, Earth science: Redox state of early magmas. Nature 480:48, 12/1/11. News. “A study of cerium in zircon minerals has allowed an assessment of the redox conditions that prevailed when Earth's earliest magmas formed. The results suggest that the mantle became oxidized sooner than had been thought.” In fact, they date the oxidation of the mantle to 4.4 billion years ago, soon after it formed. Note that the oxidation of the atmosphere was a separate process, coming 2 billion years later.

Computer resources (See web page for details and links.)

Buffers - A guide for the preparation and use of buffers in biological systems. From Calbiochem. Basic theory of acid-base buffers, but with a strong emphasis on practical information.

Electrochemical energy storage and conversion. Steve Lower offered this page of his when someone asked about the difference between a **fuel cell** and a **battery**. It is part of a broader section on “All about electrochemistry”, which is part of his Chem 1 textbook materials, listed at my site under “Other general chemistry courses”.

Electricigenic bacteria -- bacteria that can couple their electron transport directly to an external electrode, and thus can serve as the basis of a **microbial fuel cell**. One of the examples most studied is the genus Geobacter. Also see Lovley (2006).

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