

Chapters 4, 13, 15. Cracolice, 2/e. Chemistry X11.

Change of pace? Some students feel that the pace of the course changes at about this point. They feel that we “go faster” through the remaining chapters, starting with these Gas chapters. That is partly correct, so a brief comment about it here. Remember, this is a fairly short course. Throughout the course, we skip around in the book, emphasizing some core topics, covering some topics lightly, skipping others entirely. It is probably true that the amount we skip, in most chapters, is greater from here on. The purpose is so we can introduce many core ideas in the remaining time. It is quite important that you watch the handouts (and class coverage) for priorities. If you try to cover these chapters exhaustively, you can be overwhelmed. For example, right below is the “core assignment” for this group of three chapters; only 15 sections, spread over those three chapters, are assigned. Some in the class work beyond the minimum, and you are always welcome to do so. But it is particularly important in these remaining chapters that you not feel overwhelmed by the material we skip.

Chapters 4, 13, 15 (The “gas chapters”)

Core assignment:

- Ch 4: Sect 1-4
 - Ch 13: Sect 3-4, 6
 - Ch 15: Sect 1-7, 11.
- What about Ch 14? Ch 14 is actually an alternative presentation of the material in Ch 13. The authors intend that we cover either Ch 13 or 14.

⇒ There is a **practice quiz** on gas law problems posted at the web site.

You know that ordinary matter exists in three states: solid, liquid, or gas (recall Sect 2.2 & Fig 2.18). Here, we examine the characteristics of these states further, but still briefly. The most thorough analysis is possible for gases, but gas laws are fairly intuitive. They are also probably of less practical interest to most. Covering only highlights of these chapters will let us go on to more practical things, such as solutions.

You should develop an intuitive understanding of the general nature of gases, liquids and solids. This starts with the kinetic theory and the concept of ideal gases (Sect 4.2). You should understand how intermolecular forces (Sect 15.3) then lead to liquids and solids. The nature of water (Sect 15.6) illustrates these issues, and is important in its own right. *These may well be the most important sections of this assignment.*

There is a quantitative part of this material, for gases. The simple gas laws are fairly intuitive, if you understand the nature of gases. (For example, it should seem logical to you that raising the T of a gas raises its P, if all else is constant.) However, the discussion of these simple laws is interesting, because each has a good experimental basis and is also a good exercise in problem solving. We will discuss only one of these simple laws in detail: Charles’ Law, Sect 4.4. This illustrates the idea, and also serves to introduce the Kelvin temperature scale (recall Sect 3.7). The later parts of Ch 4, which we skip, introduce one other simple law, and a combined law.

Most of the core sections of Ch 13 follow on this introduction to gas quantitation from Ch 4. The ideal gas law, Sect 13.3-4, is the “ultimate” summary of (ideal) gas behavior. Sect 13.6 begins to show how to deal with gases in stoichiometry problems; the question, of course, is how to relate the convenient measurement of gas amount (volume) to the important chemical

amount (moles). Turns out... it's easy -- and is fairly easy even if you haven't followed all of the preceding gas material. Eqn 13.9 is the heart of this; the rest is practice. Also recall Ch 9 Sect 3. (The remaining sections of Ch 13, which we skip, go into other types of gas stoichiometry problems. Those who are going on in chem are certainly encouraged to work with these sections.)

⇒ ***Pitfall.*** *In doing gas law problems (Ch 4 or 13), remember that you must use the Kelvin temperature; “twice the temperature” is only meaningful on this absolute scale.*

Sect 15.1 emphasizes an important property of gas mixtures, which really follows quite logically and inevitably from Sect 4.2.

Vapor pressure (Sect 15.4) provides an example of a dynamic equilibrium; more in Ch 16 & 20.

Sect 15.9-11 deal with what happens when you add heat to a substance. The heat may raise the temperature (by an amount determined by the specific heat of the substance). Alternatively, added heat may cause a phase (state) change (e.g., liquid → gas), which occurs at constant temperature. We will examine this only briefly, focusing on the qualitative ideas in Fig 15.24.

p 416 discusses buckyballs; recall Fig 6.2e. As mentioned in the Ch 6 handout, there is a kit for making your own buckyballs at my web site, on the Download page. (It may be suitable for youngsters.)

Overview of Ch 4 & 13 (Is this helpful? Suggestions?)

This is somewhat redundant to the above, but I know students have some difficulty here deciding what is “important” as we briefly pick up the highlights of these Gas chapters. So here is another way of looking at it. (This overview does not include Ch 15.)

The general nature of (ideal) gases... The particles are far apart. They do not interact with each other (except for elastic collisions), they occupy “negligible” volume, and it does not matter which gas it is. In discussing the “amount” of such an “ideal” gas, we are interested only in the number of particles; this is usually given as n , the number of moles.

Gas pressure (P) is understood simply as the particles bouncing off the walls. There are many units, but two that are common in chemistry are the “atmosphere” and the “mm Hg” (modern name = torr). Both of these have a meaning based on simple experiment.

Cracolice introduces several units used for P (p 96). As he hints, in practice, people use various units. Even those who otherwise tend to stick to SI units may not do so for P . The main lesson for students in an intro chem course: follow your instructor's guidance about what units are preferred.

Temperature (T) is a measure of the average kinetic energy of the particles. In quantitative work, it must be expressed on the Kelvin (absolute) scale, which has a “true zero”.

The four variables that describe an ideal gas (V , T , P , n) are all related by the ideal gas law. But you should be able to understand the basic relationship between any two of the variables by an intuitive understanding of the nature of gases.

Special problem

The gas constant R is commonly given in chemistry books as $0.0821 \text{ L}\cdot\text{atm}/(\text{mol}\cdot\text{K})$ (p 352). However, you will sometimes see $R = 8.31 \text{ J}/(\text{mol}\cdot\text{K})$. What do you conclude from these statements, both qualitatively and quantitatively? Give it a try, and slip your solution in the IN envelope.

Errata and notes

p 349, Fig 13.2. Students have complained to me that this Fig is confusing. I think the reason is that the second part -- the attempt to describe what does not happen -- doesn't really work. The Fig appears to provide a particulate level description of Avogadro's law. The first part, of course, is fine. But the second part does happen -- despite the label saying it does not. That is, it happens if one looks at the balancing (the particles). If one reacts $2 \text{ mol H}_2 + 1 \text{ mol Cl}_2$, you will get precisely what is shown. The only thing that does not happen is the volume relationship, and it is not clear that is what you are supposed to see. What stands out is the collection of particles, not the volumes. The legend says "that does not happen", "clearly" referring to the previous sentence. Wrong, "it" does happen, just as described in the previous sentence.

Further reading

Books. For more about these books, see my web page of book suggestions.

C Tanford, *Ben Franklin Stilled the Waves: An informal history of pouring oil on water with reflections on the ups and downs of scientific life in general*. 1989. The central scientific story -- announced in the subtitle -- is a simple one, one observed by many from ancient times onwards. Tanford discusses this story, from early observations, including those of Benjamin Franklin, through explanation in terms of molecules and polarity -- and up through its relevance to the nature of the cell membrane. Along the way he tells us about some key scientists of the 18th-20th centuries and about the scientific environment they worked in. A delightful book.

P Forbes, *The Gecko's Foot - Bio-inspiration: Engineering new materials from nature*. 2005. The lotus leaf is easily rinsed clean; the gecko can climb a glass wall. Why? And, can we make use of the principles that Nature has used to achieve these remarkable accomplishments? Those are just two of the topics in this delightful book -- one of which is reflected in its title. The theme is bio-inspiration (sometimes called biomimetics), in which we look to Nature for an idea about how to do something. The hook-and-loop fastener, popularly known by the tradename Velcro, is an example of old, but the field has now taken on an identity that reflects a more focused effort to discover and exploit what Nature has already

learned. Some of these bio-inspiration topics deal with inter-molecular interactions, of the type discussed in Ch 15. Some of the articles listed below also deal with these topics.

Articles

P Ball, Materials science: To the heart of glass. *Nature* 421:783, 2/20/03. News. Long term disposal of radioactive waste (as at the proposed Yucca Mountain repository) is done by embedding the waste in glass. What are the long term storage issues for glass? This news story reports how study of glass from archeological samples is helpful. Some other articles on glass are at the web site, on the “Old articles” page.

C F Davidson & M R Slabaugh, Salt crystals - science behind the magic. *J Chem Educ* 80:155, 2/03. How to make alternative crystal forms of common table salt.

R S Wotton & T M Preston, Surface films: Areas of water bodies that are often overlooked. *BioScience* 55:137, 2/05. A biology article, on the special properties of the air-water interface.

P Ball, Seeking the solution. *Nature* 436:1084, 8/25/05. News feature. A discussion of the central role of water in living systems, with some consideration of whether there might be alternatives. Timely, given the current explorations of Mars - and Titan. Also see Tosca et al, 2008.

P R Sammonds, Planetary science: Creep and flow on the icy moons of the outer planets. *Science* 311:1250, 3/3/06. News. Discusses and compares ice flows on earth (glaciers, ice sheets) with those on the moons of Jupiter and other outer planets, where the ice is at much higher pressure.

P F McMillan, Solid-state chemistry: A glass of carbon dioxide. *Nature* 441:823, 6/15/06. News. “Carbon is unusual in its family of elements because it has gaseous oxides. But under high pressure, carbon dioxide forms crystalline solids and can become a glass — so revealing the chemical family resemblance.”

P S Murthy, Molecular handshake: Recognition through weak noncovalent interactions. *J Chem Educ* 83:1010, 7/06. A “Concepts in biochemistry” article. A brief overview of the importance of the issues raised in Ch 15 on “weak” bonds or “intermolecular” interactions. We introduce them in the context of boiling points, but they are involved whenever things interact. In particular, these weak interactions play critical roles in biology, including serving as the basis of how genetic information is stored in DNA and the structure of proteins.

G Tarjus, Materials science: Metal turned to glass. *Nature* 448:758, 8/16/07. News. “In order to form a glass by cooling a liquid, the normal process of solid crystallization must be bypassed. Achieving that for a pure metal had seemed impossible - until pressure was applied to liquid germanium.”

E C Fuchs et al, The floating water bridge. *J Phys D* 40:6112-4, 10/7/07. “When high voltage is applied to distilled water filled in two glass beakers which are in contact, a stable water connection forms spontaneously, giving the impression of a floating water bridge.” Yeah, right. For a quick overview that conveys the excitement and mystery of this finding, see the

news story in Nature 449:517, 10/4/07. For most of us, this is just cute, but it once again reflects the complexity of liquid water. A movie file of the water bridge is at Youtube; a link is posted on my page of Internet Resources for Intro Chem, under Water.

A L Goodwin et al, Colossal positive and negative thermal expansion in the framework material $\text{Ag}_3[\text{Co}(\text{CN})_6]$. Science 319:794-797, 2/8/08. (Also noted in Nature 451:748, 2/14/08.) Solids expand when heated? Here is an interesting exception: a solid that expands in one direction but contracts in another as it is heated. Both changes are large, and the overall result is a slight contraction upon heating. It is like flexing a lattice fence.

P W May, Materials science: The new diamond age? Science 319:1490, 3/14/08. News. Si is the basis of our modern world of semiconductor electronics. Why not C, its family member? Because the common form of C, graphite, is a good conductor. However, the less common form of C, diamond, is a semiconductor, and could potentially form the basis of the type of controlled electronics systems we associate with Si. There are major technical hurdles in making diamonds of satisfactory quality. This news story discusses the challenges, and the limited progress so far.

D Li & R B Kaner, Materials science: Graphene-based materials. Science 320:1170, 5/30/08. News. A graphene sheet is, simply, a layer of graphite -- a network of aromatic rings one atom thick. One can think of a carbon nanotube as being a graphene sheet rolled up into a tube. Graphene and nanotubes share some interesting properties, such as two-dimensional electrical conductivity (in the aromatic plane), but graphene may be much cheaper to make. This news story discusses the synthesis and properties of graphene.

N J Tosca et al, Water activity and the challenge for life on early Mars. Science 320:1204, 5/30/08. News. The common story... water is required for life; Mars has (or at least had) water; therefore Mars is (or was) suitable for life. This paper introduces a new complication: they suggest that the water on Mars may have been too salty for life. Water "activity" is a measure of water purity; the formal description of it is beyond this course. Pure water has an a_w (activity of water) = 1.0. Among earthly beings, few can grow at a_w as low as 0.9, and the lowest a_w known to support growth is about 0.6. From an analysis of the minerals found on Mars and consideration of how they must have formed, they estimate that the a_w of these waters was well below 0.9, and many were below 0.6. Now, there may be higher a_w waters they are not considering, and maybe Martian organisms are better adapted to low a_w than are Earth organisms. Nevertheless, the paper is interesting chemistry, and relevant to the consideration of life on Mars. Also see Ball, 2005.

L Qu et al, Carbon nanotube arrays with strong shear binding-on and easy normal lifting-off. Science 322:238, 10/10/08. Stickiness, or "adhesion", is a biology story as well as a chemistry story. Broadly, adhesion involves interaction between surfaces, and reversible adhesion is typically due to the types of weak bonds discussed in Ch 15. For example, lizards climbing slick walls hold on by the London (van der Waals) interactions between the wall surface and a huge number of foot hairs. In recent work scientists measured the adhesive force of a single gecko foot-hair. Many labs have been working to develop synthetic materials that mimic the gecko feet. Here, Qu et al report one that surpasses the gecko foot in some ways. Their special trick here was to curl the tips of the nanotubes.

S Granick & S C Bae, Chemistry: A curious antipathy for water. *Science* 322:1477, 12/5/08. News. A delightful overview of how water interacts with hydrophobic materials.

F Brümmer et al, Light inside sponges. *Journal of Experimental Marine Biology and Ecology* 367(2):61-64, 12/15/08. Silica is a network solid (Fig 15.22). Some deep sea sponges make silica spicules that seem remarkably like fiber optic cables. Here they show that these sponge spicules actually serve a biological role, funneling light down inside the sponge -- for the benefit of their photosynthetic symbionts, and hence for their own benefit. Of course, organisms that make silica do so under “ambient” conditions, not the harsh conditions required by chemists. A news story about this work is on my page of Internet Resources for Introductory Chemistry, under Solids.

R D Maladen et al, Undulatory swimming in sand: Subsurface locomotion of the sandfish lizard. *Science* 325:314, 7/17/09. Granular solids, such as grains of sand, “flow” -- much as liquids flow (Ch 2, question #4). Lizards “swim” through sand. This paper explores how.

D J Cole-Hamilton, Janus catalysts direct nanoparticle reactivity. *Science* 327:41, 1/1/10. News. “Metal oxide nanoparticles decorated with carbon nanotubes can be turned into readily recovered catalysts that function at the interface between oil and water phases.” That is, the particles have both hydrophilic and hydrophobic faces, so they collect at the oil-water interface.

B C Christner, Bioprospecting for microbial products that affect ice crystal formation and growth. *Appl Microbiol Biotechnol* 85:481-489, 1/10. Review. Biological materials, such as proteins or even bacteria can serve to nucleate (initiate) ice formation. Other biological materials can inhibit ice formation. Both effects have natural roles in biology -- and beyond, and both can be exploited. Among the natural roles being investigated is the effect on weather: there is increasing evidence that biological ice initiation is relevant to real-world atmospheric chemistry. This short review is a nice introduction to all these issues.

R J Saykally et al, Pinning down the water hexamer. *Science* 336:814, 5/18/12. News. Liquid water is held together by a fluctuating network of hydrogen bonds between water molecules. The time scale of H-bond fluctuations is on the order of femtoseconds -- a few picoseconds at most. And the details are still elusive. This news story discusses recent experimental work on water hexamers: clusters of six water molecules. These are fleeting structures, but they hold clues to higher order structures of water. High speed spectroscopy allows unprecedented measurements; satisfyingly, they conclude that theory and experiment are in reasonable agreement.

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

Several web sites that explore various aspects of gas behavior, often with animations.

A site on the various reference points used for STP.

Some sites about a couple of interesting liquids: Why is water blue? Snowflakes and snow crystals. Origin of water on Earth. Why is mercury a liquid? And of course, the floating water bridge, introduced above under Further reading (Fuchs et al, 2007).

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