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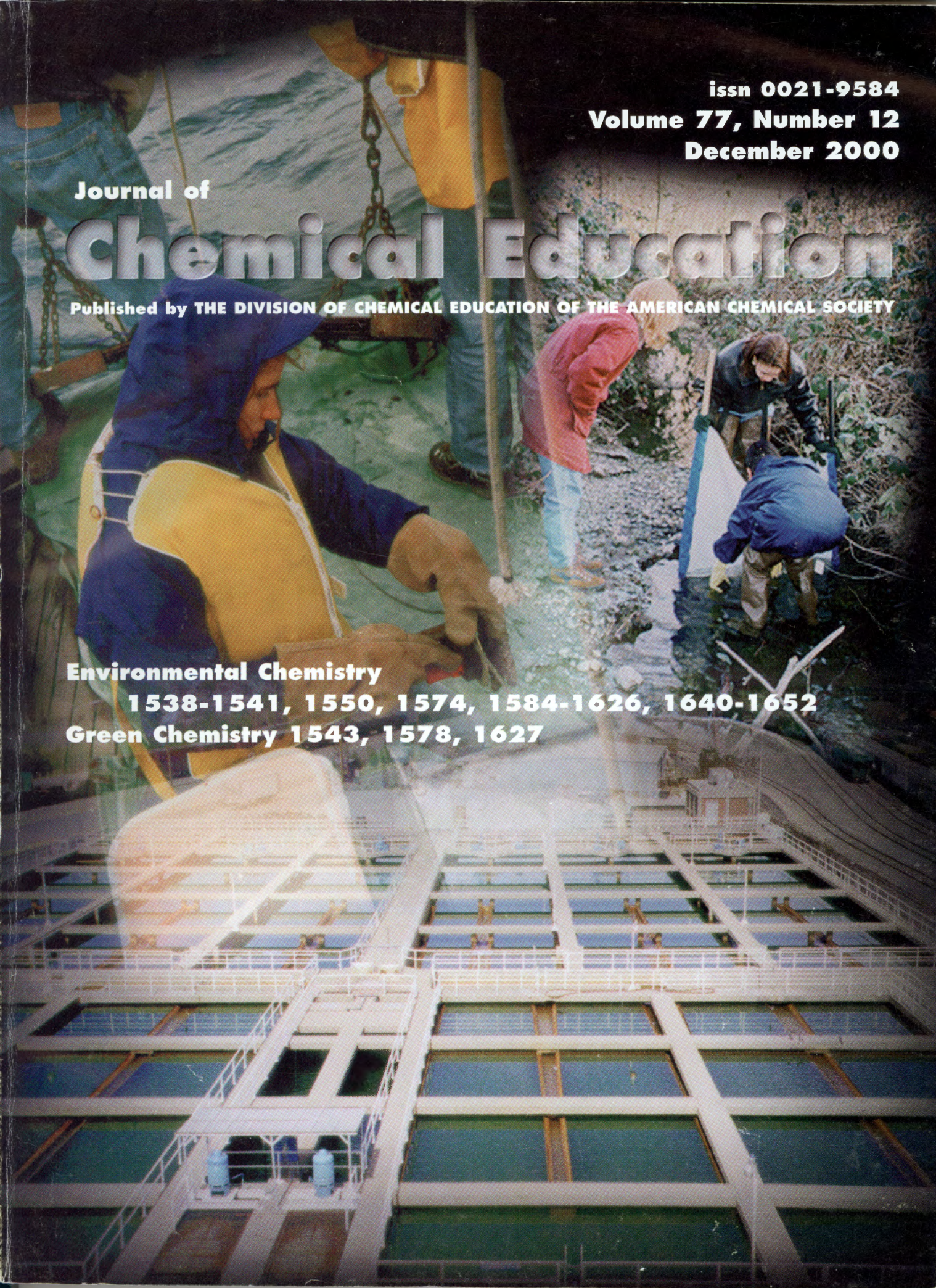
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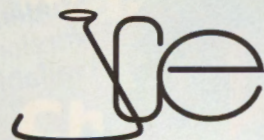
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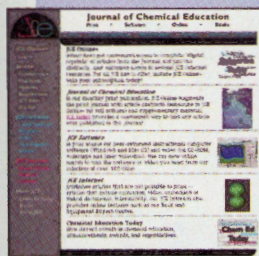
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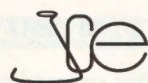


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in this issue



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Water: A Powerful Theme for an Interdisciplinary Course

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It is fitting that we start our study of chemistry with water. It is the most important substance for life as we know it. It covers 70% of the earth's surface. Its flow controls our weather, agriculture, and location of population centers. Its flow can be a source of beauty or an instrument of destruction. More regulations govern its flow than any other substance. In potable form, it looms as one of the most important substances in the 21st century: outdistancing petroleum. Finally, more chemistry has been studied using it as a solvent than any other substance. It is deserving of our study.

So begin the notes introducing first-year students to an aquatic environmental chemistry class taught at The Evergreen State College. I wrote the notes specifically for an interdisciplinary course entitled "Water". In this paper I want to describe the conception of this course, its form and content, and how the chemistry part of it was taught. The opening statement was a justification to students for what was to follow. It gives some hint of what the faculty teaching it came to realize: namely, that the topic of water was one of the most powerful integrating themes that any of us had encountered.

Context and Conception

First, it is important to understand the academic context of Evergreen. Since its inception in 1971, interdisciplinary, team-taught classes have been the rule rather than the exception. We call them academic programs. Our entry-level program for the physical sciences called *Matter and Motion* was described earlier (1). Faculty in a program teach nothing else and students enrolled in a program take nothing else. This was a particularly important factor for Water, for it meant we could go off on a four-day field trip to the Hanford Reservation or spend a week at the Friday Harbor Laboratory on San Juan Island without encountering schedule conflicts. Programs typically are year-long and have three to four faculty with a target student/faculty ratio of 23:1. When that enrollment is reached the program is closed to further enrollment.

Evergreen has specific programs that first-year students are advised to take. They are called core programs. Water was a core program. A first-year student can select from about six to eight core programs. Core programs cannot be stipulated as prerequisites for entry-level programs. So faculty in a core program are free to teach what they want without the need to cover specific topics for a later class. That is an important point for this article, for without that freedom the chemistry in Water could not have been taught the way it was.

Evergreen's location is also an important contextual factor. The college is located just outside of Olympia, the state capital. Legislation concerning water, ranging from waste-water treatment to salmon recovery to water resources and flood control, are nearly always being considered when the legislature is in session. So our students are only minutes away from observing the legislative arena where policy and science often meet. Evergreen is situated on 1000 acres with 3300 feet of shoreline on Puget Sound: the only college in the state on the Sound. We are within a two-hour drive of the Pacific Ocean, two national parks (Olympic and Mt. Rainier), and

one memorial (Mt. St. Helens). Finally, we are a day's drive from the Hanford Reservation, which is arguably the most perilous source for aquatic contamination in the country.

A geologist and I conceived Water in 1991–92 when we taught an upper-class program that integrated the two subjects, emphasizing aquatic geochemistry. We soon recognized that with just two of us the program was too narrow. The subject needed more faculty to treat more topics. We also decided it was worth trying it out on first-year students. To offer this to first-year students was not without peril, for what I had learned in 1991–92 was that the chemistry of natural systems is more complicated than the bench chemistry typically covered in introductory chemistry. This problem and how it was faced will be described later.

We designed the 1994–95 Water program based on the premise that first-year students are capable of handling more difficult tasks than we typically expect *provided* certain things are done to maintain the intensity while avoiding burnout.¹ These are to (i) have students study real systems, (ii) undertake numerous off-campus activities and frequently have relevant guest speakers, and (iii) have students be responsible for studies whose results will be significant enough that off-campus agencies will want to share the results.

I think you can sum up the provisions in two words: *significant involvement*. We believed that students could make impressive achievements if they were deeply involved in something they considered important.

In the spring before a core program is given, the faculty team for each program composes a program description for prospective first-year students. We felt it important that students be aware of the anticipated intensity of the program, so the following paragraph was added at the end of the description.

CAUTION—read before taking

Water will be a demanding class, both intellectually and physically. If you aren't prepared to devote 50 hours/week to the class you shouldn't take it. There will be exams in *Water* and lots of homework will be assigned. If you can't stand computers, you could have a problem. If you don't like being cold and wet on a field trip or splattered with Puget Sound sediment on a boat for as long as ten hours, *Water* is probably not for you. If you hate numbers, *Water* will be tough. In short, while *Water* will be a demanding class, we believe, based on our experiences, that *Water* will be a worthwhile learning experience for anyone considering a career related to the environment. But it is important that you have a realistic view of what we expect. If you are willing to work you will have our full support.

Broadcasting such an alert was not without risk. If it scared off enough students, we could lose a faculty position and the planning that went into it. To our relief, the response confirmed our basic premise. Within a week after spring pre-registration the program filled with first-year students who were not yet even on campus. By September Water had the largest waiting list of any core program.

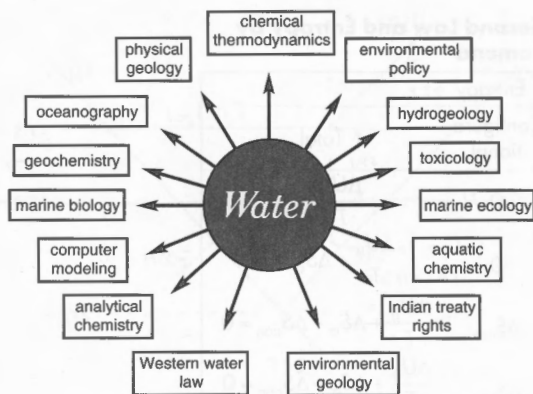


Figure 1. Summary of topics taught in the water program.

We added environmental policy, which we considered the most needed discipline, in 1994–95. We felt that environmental measurements made without knowing the laws and regulations, the responsible authorities, and the basis for their establishment lacked a crucial dimension that was as important as the numbers generated. In 1995–96 marine biology and oceanography were added. Figure 1 gives all the topics that have been included at one time or another. Some faculty taught more than one topic. For example, I taught chemistry for only two quarters, replacing it spring quarter with environmental modeling. Figure 2 lists typical off-campus activities. During a year we spent about 20 days off campus and nearly 20 speakers visited the program.

Planning a full-time multidisciplinary program is very time-consuming. The adage that the whole is greater than the sum of its parts is applicable here. Many meetings of the participating faculty during the preceding spring and summer are needed. Not only do we have to plan our own material as in a regular course, but it is important to make connections between disciplines so that the program is not just a collection of courses. This includes field trips, guest speakers, labs, and projects. Where possible, we let the system identify connections.

Form and Content

The format for teaching was the same for all the science subjects. Each faculty member had a morning each week, which consisted of 90 minutes of lecture followed by 90 minutes of a workshop where students in groups of 3–5 worked on problems or minor lab projects that related to the lecture topic. Students had one afternoon of lab each week in each science. Both in lab and especially in workshops, collaborative learning was important. There was also a weekly book seminar, which will be described later.

Deciding how to teach the chemistry in such a class was a challenge. Natural aquatic systems are complicated. To begin with, CO_2 and the accompanying carbonate equilibria are ubiquitous in natural aquatic systems. So the starting system is already a diprotic system. Consequently, a neutral system will have a pH lower than 7, which will vary depending on the partial pressure of carbon dioxide. Furthermore, natural systems are open systems (although when samples are brought into the lab and treated quickly they behave as closed systems). Redox equilibria are also complicated. Rarely is there a single reducer/oxidizer reaction. And to deal with a system like

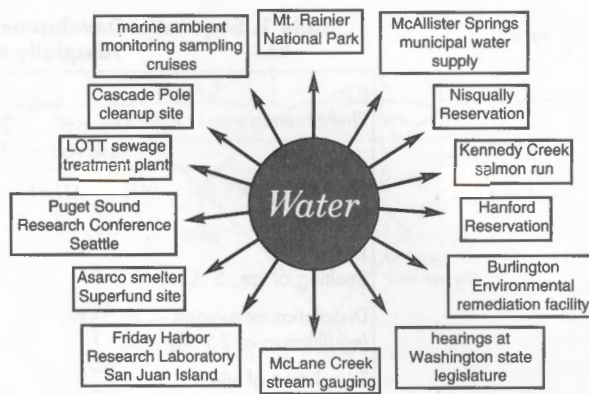


Figure 2. A listing of some off-campus activities.

sulfur, which is important for sediment chemistry, I had to use predominant area diagrams because the systems are both pH and EMF dependent. Finally, to gain a fundamental understanding of why certain things occur, for example "Why are there waterfalls but no water rises?", I introduced thermodynamics and the second law mathematically.

The chemistry that was being planned for this core program was turning out to be more complicated than students continuing the next year in *Matter and Motion* would encounter. However, core programs, which we expect first-year students to take, cannot have prerequisites. Consequently, many first-year students taking the program had never had chemistry. More problematic, however, was mathematics. We gave a diagnostic math exam during the spring and summer before classes began. It covered high school algebra, logarithms, and trigonometry (geology needed that). Depending on their performance, we advised students what they should review over the summer or whether it was even advisable to take the program. But admission to a core program cannot be denied for lack of background. As it turned out, from a class of 75 we lost perhaps 4 or 5 at the end of the first quarter. Without exception these dropouts had in common a weak math background. Attrition would have been much higher had we not offered extra remedial sessions for students who wanted them.

I know of no chemistry text that treats the topics previously mentioned that does not assume that students have already had introductory chemistry. That was worrisome. Could it be done? Sometimes I felt I was leading lambs to the slaughter. So I wrote a set of notes, which did the following:

1. "Translated" portions of Werner Stumm and James Morgan's classic *Aquatic Chemistry* (2) into concepts that a high school student could understand;
2. Employed Craig's *The Entropy Concept* (3) and Bent's *The Second Law* (4) method to develop a global approach to thermodynamics, which, for the beginner, is more understandable, including the use of entropy diagrams (5); and
3. Mixed in lightly some of Atkins's ideas on thermal entropy (6).

Most important, I chose a real aquatic system, which would allow these concepts to be introduced in an orderly manner with increasing complexity. I chose the Nisqually River. Most

Table 1. Sequential Development of the Second Law and Entropy by Nisqually River Phenomena

Phenomenon	Entropy			
	Thermal Reservoir	Structural (System)	Configurational	Total
Nahunta Falls (waterfall)	$\frac{\Delta U_{\theta}}{T} = -\frac{\Delta U_{wf}}{T}$	0	0	$\frac{\Delta U_{\theta}}{T} > 0$
Jokulhlaups (melting of ice, 5 °C)	$\frac{\Delta U_{\theta}}{T}$	ΔS_{σ}	0	$\frac{\Delta U_{\theta}}{T} + \Delta S_{\sigma} > 0$
Dissolution of oxygen (equilibrium at 25 °C)	$\frac{\Delta U_{\theta}}{T}$	ΔS_{σ}	ΔS_{con}	$\frac{\Delta U_{\theta}}{T} + \Delta S_{\sigma} + \Delta S_{con} = 0$
Dissolution of silica (equilibrium at 25 °C)	$\frac{\Delta U_{\theta}}{T}$	ΔS_{σ}	ΔS_{con}	$\frac{\Delta U_{\theta}}{T} + \Delta S_{\sigma} + \Delta S_{con} = 0$

readers of this article will have never heard of the Nisqually River. But I suspect all readers know of a body of water near their school that possesses some of its attributes.

The Nisqually begins with a roar on the southern flank of Mt. Rainier as it pours out from the terminus of the Nisqually Glacier at an altitude of about 1400 meters. After traveling 117 km it empties into Puget Sound just a few kilometers north of Evergreen. It is the only river in the country that starts in a national park and terminates in a wildlife refuge (Nisqually Delta). It is a perfect vehicle for introducing aquatic chemistry from a thermodynamic viewpoint. It begins as a very simple system chemically, becoming more complex as it wends its way to the Sound. Topically, I proceeded in the notes from a waterfall to the melting ice² to dissolved oxygen to dissolved solid to dissolved CO₂ and acid/base equilibrium to the sediments in the Sound and redox chemistry.

The Nisqually also served another purpose. Traditionally, our first field trip is to the headwaters of the Nisqually in Mt. Rainier National Park. It occurs during the second week of fall quarter, which comes in the first or second week of October. During that time of year, on a week day, we have the park almost to ourselves. By then Mt. Rainier has had a new dusting of snow. Furthermore, our purpose is more than just to observe. We also have a research permit from the Park Service to take water samples at different points along the river for measurement of temperature and pH in the field and dissolved oxygen and suspended solids at Evergreen. (This has recently been expanded to other studies). To climb down to the water's edge of a white-water river in an ancient forest on the slopes of a snow-capped mountain to collect water samples is a moving experience for students and seemed to charge up their dedication for the work that followed.

Thermodynamics and Aquatic Equilibria

A systems approach, if followed conscientiously, turns the normal sequence for introducing chemistry topsy turvy. To start, I picked a waterfall at the beginning of the river because, in my opinion, what happens in a waterfall has profound implications for chemistry yet involves no chemistry. I ask students why are there no water rises? They respond that such an event is unnatural. They have never heard of it. But the dismissal of a phenomenon based on experience alone does not help us predict what other phenomenon are unnatural. Most of the chemical reactions and processes they will

encounter in the class will be ones for which they have had no experience. What do they do then?

So we examine the waterfall more closely. I note that, as far as the conservation of energy is concerned, a water rise is possible provided the water cools down by the appropriate amount as its kinetic energy is converted to gravitational potential energy (GPE). Borrowing from Atkins, in order to understand a waterfall you have to look at it from the molecular level. As the water molecules plummet down the fall they each increase their kinetic energy in the downward direction by the same amount. Their original GPE at the top of the fall is being converted into *coherent* kinetic energy. In fact, the instant before the water hits the pool at the bottom, the conversion is complete. When the water does hit the pool a profound change occurs. Coherence is lost. The molecules are moving faster but in all directions.

To have a water rise the system would have to organize itself and redirect some of the molecules upward simultaneously. Such a reorganization is highly unlikely. And so the concept of thermal entropy is introduced. I present Clausius's definition along with how to calculate thermal entropy change at constant temperature. Table 1 shows how each successive feature of the river adds another term. The melting of ice in the river, an endothermic process, requires the introduction of the system's entropy change. Though this is a thermal energy, I refer to it as a structural energy. Next, oxygen's dissolution in water cannot be explained unless configurational entropy is introduced. Figure 3 shows the

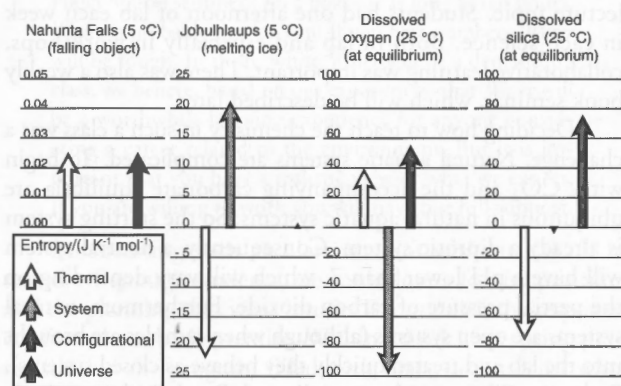


Figure 3. Entropy diagrams for the first four successive systems.

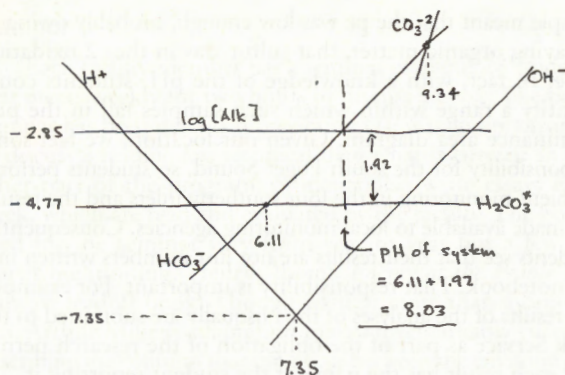


Figure 4. Hand-drawn log C diagram for open saline (19‰) system at 5 °C.

representation of these processes in terms of entropy diagrams. Entropy diagrams lend an informative graphical perspective to these new ideas.

There are two ways to approach acid/base equilibria: algebraically and graphically. My experience has been that introductory students have more difficulty with the algebraic approach because it requires the use of approximations that assume an intuition that beginning students do not have. For the simple bench systems one typically encounters in introductory chemistry texts, the algebraic method is adequate and I use it, for example, in Matter and Motion. However, in Water I used the graphical log C method first introduced to this country by Lars Sillen (7); see also Butler and Cogley (8) and Butler (9). Just as a picture may be worth thousands of words, I believe a log C diagram is worth lots of equations. It provides introductory students with a pictorial paradigm that is far easier to use and understand than a lot of equations. Aside from use of logarithms, arithmetic is as complicated as it gets mathematically. While the computer could be used for these problems, I am a believer in the "back-of-the-envelope" approach, namely, that a student should be able, on the back of an envelope or a piece of paper, to make an acid-base calculation for any system that is at least good to 0.1 pH units.

The beauty of the log C diagram (sometimes referred to as a Bjerrum plot) is that a student does not need graph paper. Furthermore, a solution consisting of a mixture of monoprotic systems plus a polyprotic system is not much more complicated using the log C approach than a single monoprotic system. The log C approach allows questions about alkalinity, open (Henry's law) or closed systems, and even ionic activity coefficients to be taken into account. And titration curves are just a simple extension (10).

Figure 4 is an example of a log C diagram, hand drawn without benefit of rulers or graph paper, for an open saltwater system (19‰ salinity) at 5 °C ($pK_{a1}^* = 6.11$, $pK_{a2}^* = 9.34$, $pK_H' = 1.27$, $pK_w' = 14.7$) exposed to the atmosphere with $P_{CO_2} = 3.14 \times 10^{-4}$ bar with an alkalinity of 1.4×10^{-3} M. The ordinate is log concentration and the abscissa, pH. From this crude figure one obtains a pH of 8.03, which is accurate to better than 0.1 pH unit. The details of how this result is obtained are explained in Note 3.

Figure 5 is the log C diagram for the system described in Figure 4 but drawn as a closed system at a temperature of

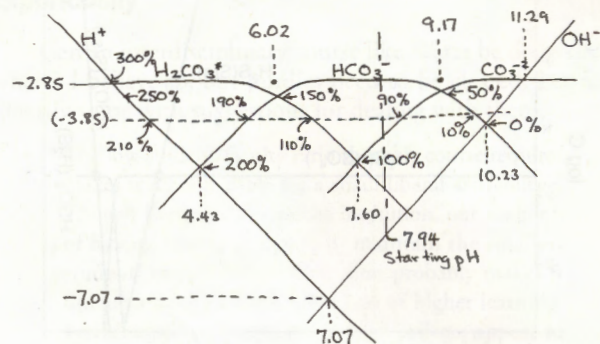


Figure 5. Hand-drawn log C diagram for a closed system with titration percentages at 20 °C.

25 °C. As in Figure 4, H^+ and OH^- are represented as activities, while other species are concentrations. Figure 5 is used to describe the titration of the sample in Figure 4 with percentages indicated for a titration at 20 °C. The details of how this result is obtained are explained in Note 4.

Once this method is understood, I can ask Water students deeper questions about acid/base equilibria than I would ask Matter and Motion students who used algebraic methods. However, it does take longer to present the graphical approach.

Using p_e , I apply the log C approach to redox systems and so students can eventually construct a 3-D (log C vs p_e vs pH) model, which, when viewed from the top, provides a predominance area diagram for the sulfur system.⁵ In Figure 6 are log C plots for the sulfur system in seawater for three pH values. The dots represent the boundary between species. Figure 7 is an overhead view of many Figure 6-like figures in which only the dots are plotted. The specific dots from the previous figure are marked. In this manner, a predominance area diagram can be constructed by a class in a workshop. An explanation of how these plots are obtained is given in Note 6.

In summary, I have found a graphical approach particularly effective in helping first-year students to not only understand complicated systems but to solve them as well.

Laboratory

Laboratory is at the heart of this program. Obviously, with as many as three sciences, it is a demanding schedule for students. In chemistry, there is an emphasis on environmental analysis. Titrations (Winkler and Gran) are performed. Trace metal analysis of Puget Sound sediments is also carried out using optical ICP spectrometry. "Ownership" of an analytical sample is deemed important. Students need to know what is involved in collecting the samples as well as analyzing them. Evergreen has two 40-ft research boats, one with a small aft laboratory and a power winch for sediment grabbers and drag nets, from which students collect water column samples using Van Dorn samplers and sediment samples using a Van Veer grabber. Sampling protocols are carefully followed.

I chose the sulfur redox system for study by the class because, on occasion, sediment samples were pulled that had a strong odor of hydrogen sulfide. This is not an indicator of fecal matter, as some students initially thought; rather, sulfur is pervasive in the aquatic environment and an odoriferous

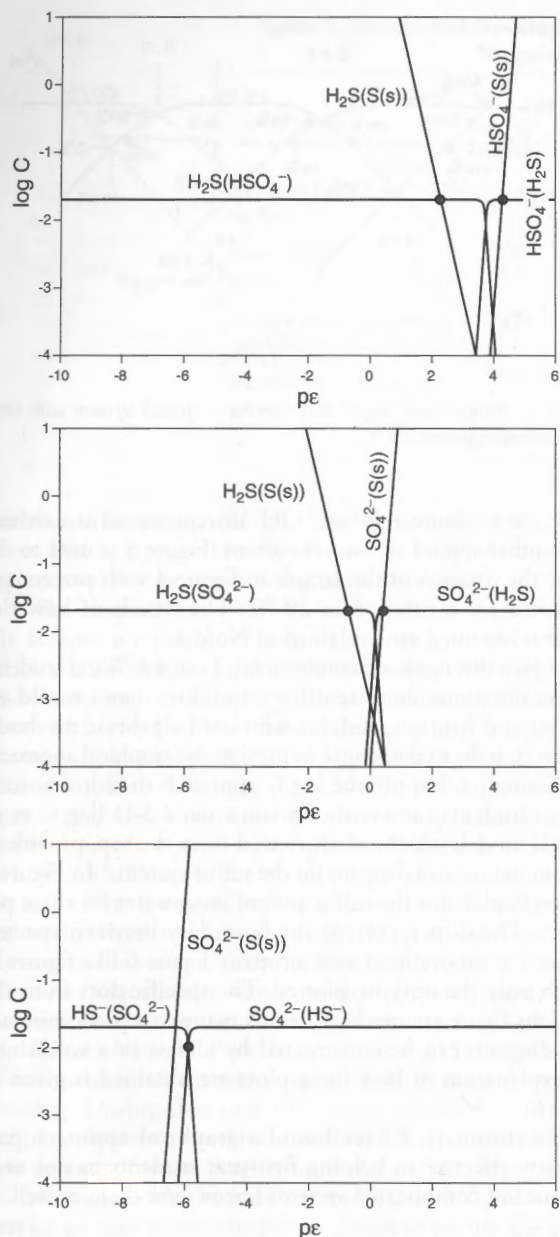


Figure 6. Log C vs pe diagrams for the sulfur system (total sulfur 0.02 M). Top: pH = 1. Middle: pH = 4. Bottom: pH = 9.

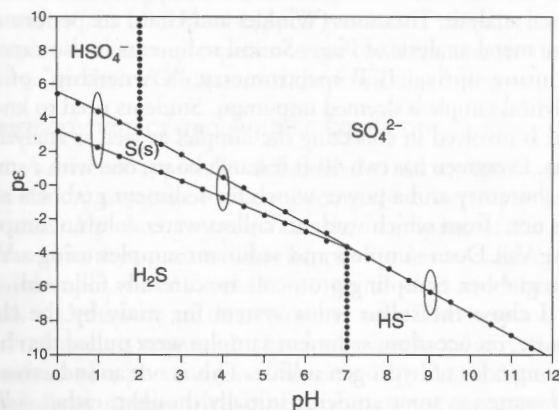


Figure 7. Predominance area diagram for 0.02 M sulfur system.

sample meant that the pe was low enough, probably owing to decaying organic matter, that sulfur was in the -2 oxidation state. In fact, with a knowledge of the pH, students could identify a range within which such samples fall in the predominance area diagram. Given our location, we feel some responsibility for the south Puget Sound, so students perform ambient monitoring in the four southerly inlets and the results are made available to local monitoring agencies. Consequently, students see that their results are not just numbers written in a lab notebook. That responsibility is important. For example, the results of the analyses of the Nisqually are submitted to the Park Service as part of the obligation of the research permit and each result has the name of the student reporting it.

A spring quarter field/laboratory project culminates the year's work. Students, in groups ranging from two to five, undertake projects whose results are of interest to some group, organization, or agency outside of the college. Students submit proposals by the end of winter quarter so that by the beginning of spring quarter each student is involved in a project that the faculty consider worthwhile and doable. Each group has a specific faculty member to oversee it. In addition to a written report, groups present oral reports, and representatives from external interested parties are invited to attend. Box 1 gives some titles of representative student projects.

Box 1. Some Representative Project Titles

- A Study of the Chemical Composition of the Lava Flows near Mt. St. Helens (4)
- Bioassessment of Henderson Inlet (Marine Ambient Monitoring Program) (3)
- Microalgae (3)
- A Study of *spartina alterniflora* Growth Rates in the Niiwaki River Area of Willapa Bay, Washington (3)
- Study of Lead and Cadmium in Drinking Water on the Evergreen Campus (4)
- Effects of Logging on Watersheds (5)
- Impact of Pinnipeds on Salmon (4)
- Study of Metal Content in Sediments of Gull Harbor (2)
- Distribution of Bivalves in Eld Inlet (3)
- Distribution of Blue Mussels (3)
- Marine Ambient Monitoring Program: Benthic and Sediment Assessment (5)
- Salinity and Metal Precipitation in the McAllister Creek Estuary (3)
- Contamination of Shellfish (3)
- Epidemiological Assessment of Effects of Contaminated Sediments on Squaxin Indian Tribe (3)
- Study of Oyehutt Creek, Ocean Shores (3)
- An Examination of Eutrophication and the Trophic Status of Lake St. Clair (5)
- Contaminant Deposition in the Soil of Yauger Park (2)
- A Baseline Analysis of Background Contamination Levels in the Area Surrounding Manning Stables (3)

Note: The number of students in the group is shown in parentheses.

Seminar

Each faculty member has a seminar of about 23 students that meets weekly for two hours to discuss a book. The book seminar has been described previously (1); it is an opportunity to discuss a reading less technical than what is covered in the other part of the program. Students also write essays each week, which are read and evaluated by the faculty. The books used for the seminar vary from year to year but a few are worth mentioning. Henrik Ibsen's *Enemy of the People* is a stalwart leadoff book. Though written more than a century ago, Arthur Miller's adaptation makes it remarkably current, describing the collision that can occur between the environment and jobs—in this case, because of water. Marc Reisner's *Cadillac Desert*, which chronicles the historical development of water resources in the West, and Bruce Brown's *Mountain in the Clouds*, which covers problems with salmon, are both worthwhile. We have also used classics such as Aldo Leopold's *Sand County Almanac* and Rachel Carson's *Silent Spring*. Box 2 lists some books that have been used for seminar.

Box 2. Representative Books Used in Seminar

Edward Abbey. *Down the River*; Penguin, 1982. A series of essays concerning western water by a self-proclaimed "agrarian anarchist".

Bruce Brown. *Mountain in the Clouds*; University of Washington Press, 1995. A thoughtful analysis of the decline of the wild Pacific salmon.

Rachel Carson. *Silent Spring*; Houghton Mifflin, 1962. The book that introduced the environment as a political issue.

Al Gedicks. *The New Resource Wars*; South End Press, 1992. A documented analysis of some environmental conflicts in the Midwest.

Tom Harris. *Death in the Marsh*; Island Press, 1991. A story of the selenium problem in water in America.

Vi Hilbert. *Haboo*; University of Washington Press, 1985. Native American stories from Puget Sound translated into English.

Ivan Illich. *H₂O and the Waters of Forgetfulness*; Heyday Books, 1985. A philosopher's view of water.

Aldo Leopold. *A Sand County Almanac*; Oxford University Press, 1949. A classic, describing the natural world by someone who truly related to it.

Martin Lewis. *Green Delusions*; Duke University Press, 1994. A critique of radical environmentalism.

John McPhee. *Encounters with the Archdruid*; The Noonday Press, 1971. A narrative of conversations/arguments during journeys of David Brower with three environmental developers.

Arthur Miller/Henrik Ibsen. *An Enemy of the People*; Penguin, 1979. Miller's adaptation which treats what happens when truth and the will of the majority collide.

John Nichols. *The Milagra Beanfield Wars*; Henry Holt, 1994. A humorous novel about water rights in a small town in the rural Southwest.

Brenda Peterson. *Living By Water*; Alaska Northwest Books, 1990. Essays concerning water's spiritual impact on the author.

Marc Reisner. *Cadillac Desert*; Penguin, 1993. An engaging history of the use and misuse of water in the Southwest.

Aubrey Wallace. *Eco-Heroes*; Mercury House, 1993. Twelve biographies of environmental activists from around the world.

Exportability

Can an interdisciplinary course like *Water* be done elsewhere? I believe so, but hurdles need to be cleared. Let me identify some with suggestions for dealing with them.

- The low student/faculty ratio that this course requires makes it more feasible for a small liberal arts college. Though Evergreen is a public institution, our tradition of having first-year programs maintain the smallest student/faculty in the curriculum probably makes it unique among public institutions of higher learning. Interdisciplinary programs at small colleges appear to be becoming more common.
- A departmental structure and the territorialism that accompanies that will always put interdisciplinary ventures at risk. But there are ways to deal with this. First of all, the subjects offered should have a content that will allow students taking them to skip some if not all of the department's introductory course. So a faculty member in an interdisciplinary course is preparing students for a major in that department. (My earlier experience at a traditional liberal arts college pointed out the need to find faculty in other key disciplines who are supportive of interdisciplinary teaching. The good news is that faculty and college administrators seem much more supportive of such ventures than they were 10 or 15 years ago and many successful efforts have been reported in this *Journal* (11–16). From a career point of view, it must be recognized that what students see faculty doing in organizing and interconnecting to present such a course is what they, the students, will more and more be expected to do when they enter the profession.
- The 100% commitment of students and faculty to a single course may be a hard sell at some institutions but I believe it is crucial. The situation at every institution is unique, but if this is a sticking point in the beginning it does not have to be a year-long course. A semester could do, although a quarter would be too short. Also, faculty could cycle through for a quarter or semester at a time that would allow more exposure to more disciplines.
- Finally, I want to reiterate the inherent inefficiency in producing an interdisciplinary course. Many faculty will find the amount of time required to plan a joint interdisciplinary course frustrating compared to offering a course on their own. To ease the strain of the first offering, try to convince either your administration or a foundation to support the planning for the first start-up. The incentive for the administration is enrollment. Interdisciplinary courses can be very popular, particularly those with an environmental-outdoor-substantive project content. Such a course could be an important recruitment instrument for students both for the institution and for departmental majors.

Conclusions

One may ask about the repetition that students experience who take *Water* their first year and then the entry-level program, Matter and Motion (M&M) the next. It has been our experi-

ence that repetition is not bad. When Art Campbell was asked when chemical kinetics should be taught, he answered "Early and often". I believe the same can be said of much of chemistry. Students coming from Water have a global view of thermodynamics and a pictorial view of chemical equilibrium. In M&M they are presented with the traditional, system-centered view of thermodynamics and an algebraic view of equilibrium. Students who experience both can select those tools and concepts that work best for them.

Water has continued to be a popular offering both for faculty and students. While its name and content have changed from year to year, its basic philosophy remains the same. For me, it is one of the most important classes that I have taught. It attracts so many different disciplines. In fact, a planning issue is the balance between the number of disciplines to be included against the 23 students that the program must add for every faculty member who joins it. But the connections that can be made between chemistry, geology, environmental policy, biology, mathematics, and computer programming are important and exhilarating for students and faculty.

Acknowledgments

What I accomplished in the Water program would not have been possible without the other faculty who taught with me. I gratefully acknowledge their support: Jude Van Buren, biology and public policy; Cheri Lucas-Jennings, environmental policy; Gerardo Chin-Leo, marine biology; and Jim Stroh and Ken Tabbutt, geology.

Notes

1. Student burnout is an important consideration for faculty planning when designing a full-time program.

2. I exercised editorial license by having ice melt after the waterfall and well after the glacier melted to produce the river by invoking a Jökulhlaups, an Icelandic term, describing a phenomenon that occurs occasionally when large quantities of water, ice, and rock are released all at once and roar down the river for miles.

3. *The Open-System log C Diagram.* First, draw H^+ and OH^- lines to establish reference points. The $H_2CO_3^*$ line refers to the mixture of dissolved carbon dioxide, which predominates, and carbonic acid. Unless you are considering kinetics, there is no point separating them. Henry's law tells us that the $H_2CO_3^*$ line is flat regardless of pH.

$$K_H = \frac{[H_2CO_3^*]}{p_{CO_2}} \quad \text{where } [] \text{ represents concentration}$$

We know that $[HCO_3^-]$ must cross the $[H_2CO_3^*]$ line with a slope of +1 when $pH = pK_{a1}^{*}$. The composite pK_{a1}^{*} corrected for ionic effects involves concentrations, not activities, of acid/base conjugates and can be determined from the thermodynamic K_a by a simple correction (see 2, pp 102–105; or better, pp 204–207 of the 2nd edition.)

$$K_{a1}^{*} = \frac{a_{H^+}[HCO_3^-]}{[H_2CO_3^*]}$$

Carbonate will cross $[HCO_3^-]$ with a slope of 2 at $pH = pK_{a2}^{*}$. That completes the log C diagram.

To find the pH we find the dominant intersection that satisfies the electroneutrality expression (EE), which is

$$[Alk \text{ or } Na^+] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$

Inspection of the logC diagram allows it to be simplified to

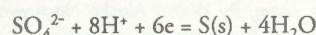
$$[Alk \text{ or } Na^+] = [HCO_3^-] + 2[CO_3^{2-}] = 1.4 \times 10^{-3} M$$

Using 6.11 as pK_{a1}' (5 °C and 19‰ salinity), $p_{CO_2} = 10^{-3.5}$ atm, and Henry's constant equal to $10^{-1.27}$, we obtain $\log [H_2CO_3^*] = -4.77$. Since $\log [Alk] = -2.85$, the $[Alk]$ line intersects the HCO_3^- line 1.92 log units above that. Therefore the dominant intersection for the electroneutrality expression is $[Alk] = [HCO_3^-]$. All other species in the EE lie well below this intersection. To reach the intersection from the known intersection at $pH = 6.11$ we have to go up 1.92 log units on the HCO_3^- line. Since the slope is +1, we have to go that much higher in pH as well. So the $[Alk]$ crosses $[HCO_3^-]$ at a pH of $6.11 + 1.92 = 8.03$. The dominant carbon species under these conditions is HCO_3^- .

4. *Closed System Titration (Fig. 5).* A sample of the solution in Figure 4 is brought into the lab for a titration (Gran) with strong acid. Assume that the salinity remains the same but the temperature rises to 20 °C. The alkalinity does not change because it is a conservative property, but the pH will change because the equilibrium constants change. Assume further that the analysis in the lab occurs too fast for equilibration with the atmosphere so it is a closed system. Figure 5, a closed-system log C diagram, reflects that. $[H_2CO_3^*]$ is no longer fixed. The new pK_a' values at 20 °C and 19‰ salinity are $pK_{a1}' = 6.02$, $pK_{a2}' = 9.17$, $pK_w = 14.14$. Since alkalinity is conserved the ratio of $\log([HCO_3^-]/[H_2CO_3^*])$ remains the same at 1.92. That puts the initial pH of the solution at 7.94 (6.02 + 1.92). Percentages can be quickly drawn for the titration of a pure solution of CO_3^{2-} of the same analytical concentration, where each equivalence point is denoted by successively larger 100%. The midpoints in the titration (50%, 150%) occur at the intersections falling directly under the system points at the respective pK_a' values. A line drawn 1 log unit down from $\log C = -2.85$ creates five intermediate percentages that key off the system points: 10% would occur at $pH = 10.17$ (9.17 + 1.00), 90% at $pH = 8.17$ (9.17 – 1.00), etc. Just from this crude drawing one can see that this titration would begin somewhere between 90 and 100%; that is, just before the first equivalence point for a pure solution of carbonate. It occurs at 94%, to be exact (7.94 – 9.17 = –1.23, so $10^{-1.23} = 0.058$ and $1 - 0.058 = 0.941$).

5. I have found the construction of 3-D models in workshops an effective way for students to understand phenomena that are dependent on more than one independent variable. Students plot lines or points on a transparency that has coordinates already printed on it. Important intersections are marked with brightly colored stick-on circles. The transparencies are attached to a thin Lucite sheet and the sheets are mounted in a Lucite frame. After several sheets are in place, the viewer can see patterns in three dimensions, which would have gone unnoticed in two dimensions.

6. *pE and Predominant Area Plots (Figs. 6 and 7).* The treatment of redox equilibria parallels the acid/base log C method where the reduction half-reaction is the analog of the K_a expression and $pE = -\log[e^-]$ is the analog of pH. (When first introduced to it, many, like me, will object to a $\log [e^-]$ term. While one could argue that it is little worse than $pH = \log [H^+]$, the important point is that, as a computational tool, it works.) Take for example the reduction of sulfate to solid sulfur.



If we define

$$K_{SO_4^{2-}/S(s)} = \frac{1}{[SO_4^{2-}][H^+]^8[e^-]^6} = \exp\left[\frac{nE_{SO_4^{2-}/S(s)}^\circ}{0.0591}\right] = 36.2$$

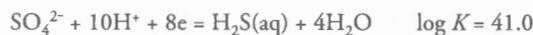
(at 25 °C), then, rearranging,

$$[e^-]^6 = \frac{1}{K_{\text{SO}_4^{2-}/\text{S(s)}} [\text{SO}_4^{2-}] [\text{H}^+]^8}$$

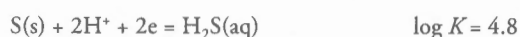
taking negative logs and multiplying by -1 and rearranging yet again we have

$$\text{p}\epsilon = \frac{36.2}{6} + \frac{1}{6} \log [\text{SO}_4^{2-}] - \frac{8}{6} \text{pH}$$

So the plot of $[\text{SO}_4^{2-}]$ versus the master variable, $\text{p}\epsilon$, is a straight line with a slope of +6. $\text{p}\epsilon$ expressions for the other redox reactions are given below.



$$\text{p}\epsilon = \frac{41.0}{8} + \frac{1}{8} \log \frac{[\text{SO}_4^{2-}]}{[\text{H}_2\text{S}(\text{aq})]} - \frac{10}{8} \text{pH}$$



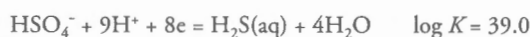
$$\text{p}\epsilon = \frac{4.8}{2} - \frac{1}{2} \log [\text{H}_2\text{S}] - \text{pH}$$



$$\text{p}\epsilon = \frac{34.2}{6} + \frac{1}{6} \log [\text{HSO}_4^-] - \frac{7}{6} \text{pH}$$



$$\text{p}\epsilon = \frac{34.0}{8} + \frac{1}{8} \log \frac{[\text{SO}_4^{2-}]}{[\text{HS}^-]} - \frac{9}{8} \text{pH}$$



$$\text{p}\epsilon = \frac{39.0}{8} + \frac{1}{8} \log \frac{[\text{H}_2\text{S}]}{[\text{HSO}_4^-]} - \frac{9}{8} \text{pH}$$

Expressions for logarithmic concentrations can be obtained from the above equations. For redox couples where one member is solid, a straight line is obtained. When both are soluble, plots similar to acid/base couples are produced. But several lines (half-reactions) can represent the same species, so it is important to note the other member of the couple when representing a species. One then selects which line to use in the following manner. For example, in the middle panel of Figure 6 ($\text{pH} = 4$), if we start at the far right (high $\text{p}\epsilon$) we have two lines representing sulfate. But the one with respect to solid sulfur, $\text{S}(\text{s})$, requires a sulfate concentration that far exceeds the 0.02 M that the system has. So solid sulfur cannot exist under these conditions and the lower couple $\text{SO}_4^{2-}/\text{H}_2\text{S}$ must obtain. The

dominant species is sulfate. As we move toward the left we eventually reach a $\text{p}\epsilon$ where the $\text{SO}_4^{2-}/\text{S}(\text{s})$ has dropped sufficiently to cross the $\text{SO}_4^{2-}/\text{S}(\text{s})$ line, so solid sulfur forms at this point. Mark that intersection as the $\text{p}\epsilon$ where solid sulfur becomes dominant. A similar conclusion can be made with respect to H_2S if we move from the far left to the right. The requisite $[\text{H}_2\text{S}(\text{aq})]$ for solid sulfur to exist is too large until the line intersects the $\text{H}_2\text{S}/\text{SO}_4^{2-}$ line. Therefore that intersection marks the boundary between H_2S and $\text{S}(\text{s})$.

At $\text{pH} 1$ (Fig. 6, bottom panel) the $\text{S}(\text{s})/\text{SO}_4^{2-}$ line has shifted relative to the $\text{SO}_4^{2-}/\text{HS}^-$ system so that it is impossible for it to cross the $\text{SO}_4^{2-}/\text{HS}^-$ line. As a result, solid sulfur can never exist when HS^- predominates (except, of course, at that single point where all four coexist).

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