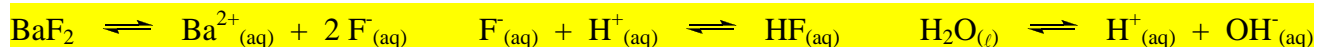


## Lecture Notes – Chem 222 – Systematic Treatment of Equilibria – Rob Rossi

On the Friday before break, Professor Kuwata wrapped up by introducing a scary prospect, which may have haunted your nightmares over the whole of the break...or which you may have completely forgotten about while lounging on the beach. He pointed out that in calculating the aqueous solubility of  $\text{BaF}_2$  in 0.10M NaF, the basicity of  $\text{F}^-$  may have an important effect:



This is a relatively simple example of a more general problem: in any chemical system, there can be any number of chemical reactions taking place, *each* of which must reach equilibrium before the system will be at equilibrium...and often, the equilibria interact with each other, as do the three above.

### SYSTEMATIC TREATMENT OF EQUILIBRIUM – HARRIS, CH 8, §8-4 AND 8-5

To deal with the general case, a more systematic approach can prove helpful, and Harris introduces this (in Chapter 9) as the "Systematic Treatment of Equilibrium." The goal is to provide a means of tackling any equilibrium problem, no matter how complicated. The first key concept related to this is

#### Degrees of freedom

$$n_{\text{df}} = (\# \text{ of variables}) - (\# \text{ of independent equations involving those variables})$$

If  $n_{\text{df}} = 0$ , the system is "fully specified" and, in principle, any unknown variables can be calculated. If all the equations are linear, there is one and only one solution, while if any of the equations are nonlinear, there may be any number of solutions, including none. If  $n_{\text{df}} > 0$ , the system is "underspecified" and there is no point in trying to find a solution, because many values for the variables will satisfy the constraints specified on the system. (How many males are there in a school of 54 fish?) If  $n_{\text{df}} < 0$ , the system is overspecified, and the equations you think are all independent really aren't, or they are logically/physically incompatible (they can't all be satisfied at once). [How many males are there in a school of 54 fish? Half the fish are male, and 14 are female.] {Ummm...no neuter fish.}

*There's no point in trying to solve a complex system of equations until you have confirmed the equations are all independent, calculated  $n_{\text{df}}$ , and confirmed that it is zero.*

Next, there are a few "balances" that must be satisfied for any (realistic) physical system, and these are handy because they can be readily written out and used to help solve any chemical problem. The first is

#### Charge Balance

$$\sum_{\text{phase}} \text{charge} = 0 = \sum_{\text{phase}} [\text{positive charges}] - \sum_{\text{phase}} [\text{negative charges}] \Rightarrow$$

$$\sum_{\text{phase}} [\text{positive charges}] = \sum_{\text{phase}} [\text{negative charges}]$$

While this is not true to the last electron (static charges can build up on stuff), the net charge on any chemical system has to remain very close to zero, lest its container go hurtling through space toward the countervailing charge or lightning bolts strike between them in order to cancel out the difference. (Put another way, the average real-life lightning bolt carries a charge of 5 Coulombs: 52  $\mu\text{mol}$  of electrons.)

Charge balance must simultaneously apply for each phase in a system; but we generally don't gain much by writing it for the solid phase. Doing so for the liquid phase of the example from last Friday, we get:

$$0 = (+2)[\text{Ba}^{2+}] + (+1)[\text{Na}^+] + (+1)[\text{H}^+] + (-1)[\text{OH}^-] + (-1)[\text{F}^-]$$
$$\Rightarrow 2[\text{Ba}^{2+}] + [\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{F}^-]$$

### Atomic ("Mass" or "Material") Balance

Chemical reactions can't create, destroy, or change the atomic number of atoms. Consequently, the number of atoms of a given type must be conserved across any chemical change. Specifically,

$$[\# \text{ of atoms of A present}]_{\text{initial}} = [\# \text{ of atoms of A present}]_{\text{equilibrium}}$$

An atomic balance can be written for each element present in a chemical system, but you should only write as many as you need to fully specify the problem. If you write out every last one, typically the last one will not be independent of the charge balance, which is generally easier to write.

To illustrate, I'm actually going to go through and write out an atomic balance for each element present in our sample system, and then show you that one of them is not independent. In doing so, we need to keep in mind that we have some solid  $\text{BaF}_2$  at the bottom of the beaker, and a bunch of water everything is swimming around in. We want to visualize the beaker both initially, and at equilibrium:

Initially present/added	Present at equilibrium
$0.10 \text{ M Na}^+_{(\text{aq})}$	$[\text{Na}^+]$
$0.10 \text{ M F}^-_{(\text{aq})}$	$[\text{F}^-]$
$[\text{BaF}_{2(\text{s}), \text{initial}}]$	$[\text{Ba}^{2+}], [\text{BaF}_{2(\text{s}), \text{equil}}]$
$[\text{H}_2\text{O}_{(\text{l}), \text{initial}}]$	$[\text{H}^+], [\text{OH}^-], [\text{HF}], [\text{H}_2\text{O}_{(\text{l}), \text{equil}}]$

Atomic balances

$$\text{Na initially present} = F_{\text{NaF}} = 0.10 \text{ M} = [\text{Na}^+] = \text{Na present at equilibrium, once BaF}_2 \text{ has dissolved}$$

$$\text{All forms of Ba initially present} \Rightarrow [\text{BaF}_{2(\text{s}), \text{i}}] = [\text{Ba}^{2+}] + [\text{BaF}_{2(\text{s}), \text{e}}] \Leftarrow \text{All forms of Ba at equil.}$$

$$\text{Balance on F: } 2[\text{BaF}_{2(\text{s}), \text{i}}] + F_{\text{NaF}} = [\text{F}^-] + [\text{HF}] + 2[\text{BaF}_{2(\text{s}), \text{e}}]$$

$$\text{Balance on O: } [\text{H}_2\text{O}_{(\text{l}), \text{i}}] = [\text{OH}^-] + [\text{H}_2\text{O}_{(\text{l}), \text{e}}]$$

$$\text{Balance on H: } 2[\text{H}_2\text{O}_{(\text{l}), \text{i}}] = [\text{HF}] + [\text{OH}^-] + [\text{H}^+] + 2[\text{H}_2\text{O}_{(\text{l}), \text{e}}]$$

Ok, the systematic approach would then call upon us to translate each chemical reaction into mathematical terms as well. Let's set aside activity for the moment (this will generally be called for in at least the first attempt at solving any problem requiring the systematic approach):

$$\text{Solubility product of BaF}_2: [\text{Ba}^{2+}][\text{F}^-]^2 = 1.7 \times 10^{-6}$$

$$\text{Autoionization of water: } [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

$$\text{Acid dissociation constant of HF: } \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = 6.8 \times 10^{-4}$$

Very good, now let's see if we have a solvable system. We want to make the system of equations we have to solve as simple as possible, so what if we use just the three equilibrium expressions above, the charge balance, and the atomic balance on sodium? Our variables in that case would be

$$\text{Variables: } [\text{Ba}^{2+}], [\text{Na}^+], [\text{H}^+], [\text{OH}^-], [\text{F}^-], \text{ and } [\text{HF}] \Rightarrow 6 \text{ variables}$$

$$\text{Equations: } 3 \text{ equilibria, charge balance, Na atom balance} \Rightarrow 5 \text{ equations}$$

$$n_{\text{df}} = (\# \text{ of variables}) - (\# \text{ of independent equations involving those variables}) = 6 - 5 = 1$$

If we weren't worrying about the basicity of  $\text{F}^-$ , we'd be fine, but we have  $[\text{HF}]$ , so we're underspecified.

We'd do best by selecting just one more atomic balance, one that doesn't introduce any new variables...but all of them do. In fact, even if we take *all* of them into account, we seem under-specified:

$$[\text{Ba}^{2+}], [\text{Na}^+], [\text{H}^+], [\text{OH}^-], [\text{F}^-], [\text{HF}], [\text{BaF}_{2(s), i}], [\text{BaF}_{2(s), e}], [\text{H}_2\text{O}_{(l), i}], \text{ and } [\text{H}_2\text{O}_{(l), e}] = 10 \text{ variables}$$

With only nine equations (3 equilibria, the charge balance, and 5 atomic balances),  $n_{df}$  is still one. Ah, but this is because we truly do have an underspecified system! We could add any amount of solid  $\text{BaF}_2$  in excess of its solubility, and the system could reach equilibrium. There isn't a single answer for  $[\text{BaF}_{2(s), i}]$  that's going to emerge from all this. We can deal with this in two ways:

1. Define a *basis* – we don't really care about how much  $\text{BaF}_2$  we start with, so just pick an arbitrary amount that makes sense: say 0.1 mol per liter of the stuff, in this case.
2. Use algebra and "chemical intuition" to eliminate the variables of non-interest from the system of equations

In my chemical engineering days, I'd have always gone with (1), but now I'm a chemist, so let's take that approach. It can be aided by chemical intuition (i.e., understanding chemistry!): While nature doesn't set specific allowed values for  $[\text{BaF}_{2(s), i}]$  and  $[\text{BaF}_{2(s), e}]$ , it *does* set  $([\text{BaF}_{2(s), i}] - [\text{BaF}_{2(s), e}])$ , which is really just the solubility of  $\text{BaF}_2$ . So we should find that combining those two variables as their difference should lead to some simplification, and indeed it does:

$$[\text{BaF}_{2(s), i}] - [\text{BaF}_{2(s), e}] = [\text{Ba}^{2+}]$$

$$2[\text{BaF}_{2(s), i}] - 2[\text{BaF}_{2(s), e}] + 0.10 \text{ M} = [\text{F}^-] + [\text{HF}]$$

That means that the atomic balances on Ba and F can be reduced to  $2[\text{Ba}^{2+}] + 0.10 \text{ M} = [\text{F}^-] + [\text{HF}]$ , which is one additional equation that doesn't introduce any additional variables, and would suffice to make our system fully specified, with  $n_{df} = 0$ , and soluble. This equation is something we could really have come up with directly, rather than going through atomic balances: it states that, effectively, the total amount of  $\text{F}^-$  in solution is the amount provided by the dissolution of  $\text{BaF}_2$  plus the amount provided by  $\text{NaF}$ , and that it must all be present as either  $\text{HF}$  or  $\text{F}^-$ . Similar algebra on the oxygen and hydrogen balances can lead to a similar expression, one which chemical intuition could also provide:

$$[\text{H}_2\text{O}_{(l), i}] - [\text{H}_2\text{O}_{(l), e}] = [\text{OH}^-]$$

$$2[\text{H}_2\text{O}_{(l), i}] - 2[\text{H}_2\text{O}_{(l), e}] = [\text{HF}] + [\text{OH}^-] + [\text{H}^+]$$

$$\Rightarrow 2[\text{OH}^-] = [\text{HF}] + [\text{OH}^-] + [\text{H}^+] \Rightarrow [\text{OH}^-] = [\text{HF}] + [\text{H}^+]$$

This is saying, in essence, that all the protons in solution come from the dissociation of water – and they are either floating around free, or tied up by  $\text{F}^-$  ions as  $\text{HF}$ . We could have come up with it directly.

Now, if we want to solve this problem, we don't want to try using *both* of the combined atomic balances above and the charge balance! That would give us an overspecified problem, with  $n_{df} = -1$ . Why's that? Well, because with one of the two equations above and the charge balance, the other can be derived:

$$2[\text{Ba}^{2+}] + [\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{F}^-]$$

$$2[\text{Ba}^{2+}] + [\text{Na}^+] + [\text{H}^+] = [\text{HF}] + [\text{H}^+] + [\text{F}^-]$$

$$2[\text{Ba}^{2+}] + [\text{Na}^+] = [\text{HF}] + [\text{F}^-]$$

So, the charge balance and these two equations are not *independent* – the third can be derived from either of the other two. If we tried to solve the system using all of them, we'd keep getting things like  $[\text{HF}] = [\text{HF}]$ , or in other words,  $0 = 0$ . We'd find ourselves going in circles...so we want to let  $n_{df}$  be our guide, and pick two. Which two? Choose the two that simplify the math the most. In this case I've

already crunched the atomic balances down to simplicity, so I'll use them. But if I weren't demonstrating overspecification, I'd have stopped with the charge balance and Ba+F balance equations.

This isn't an algebra, applied math, or computer science course, so I'm not going to spend a lot of time going through how one could actually solve this system of equations. Usually, a combination of algebra and iteration is required, and the latter can be done by hand, with a calculator, or with a computer. I'll take the time to show you a few tricks for doing this sort of thing in Excel:

1. Name cells using the name box in the upper left corner of the spreadsheet: select the cell, replace the A1-type name with one of your own, and hit enter
2. Naming labeled cells using the Insert:Names:Create function (works with or without = sign)
3. Enter the equations in the form  $f([\text{I}]'s) = \text{a constant}$ ; if one of these constants is many orders of magnitude different from the others, you may need to invert that equation to help Excel out
4. Start up Excel's Solver. Blank out the target value cell and enter each equation as a constraint
5. In the options for the solver, set convergence to  $1e-24$  and solve (if no solution, see 8)
6. Gradually add leading zeros to the precision, under solver options, solving after each addition
7. If needed, try toggling the solver options "Assume non-negative" and "Use automatic scaling"
8. If solution is not found: 1) Check equations are valid 2) Try tweaking guess values slightly (if you resort to this, you may have to re-set precision to a larger value, as well)
9. Continue cranking down precision and solving until desired precision in results is reached

Concrete example using Equation Solver Spreadsheet (guess values) [DO NOT SAVE AT END!]:

1. Converge to  $1e-24$  and solve without changing any other options  $\Rightarrow$  works, but imprecise
2. Add 1 zero to precision and solve  $\Rightarrow$  works, result is a bit closer to believable
3. Add another zero to precision and solve  $\Rightarrow$  fails, "Can't find feasible solution." CANCEL
4. Add auto-scaling and solve  $\Rightarrow$  fails, CANCEL
5. Add assume non-negative and solve  $\Rightarrow$  works, close enough? Probably, but for sake of example
6. Add another zero to precision and solve  $\Rightarrow$  fails, our friend "Can't find feasible solution"
7. Uncheck auto-scaling and assume non-negative, solve  $\Rightarrow$  works
8. Add another zero to precision and solve  $\Rightarrow$  fails, our friend "Can't find feasible solution"
9. Round off H guess value to  $8.15E-9$  and solve  $\Rightarrow$  works (other tricks above would fail)
10. Could continue indefinitely, but it gets progressively harder, and nothing is gained. (All concentrations have now converged to within 2 SF, the precision of the equilibrium constants.)

Another approach involves algebraically reducing system of equations to one equation in one variable, and solving (graphically, with a calculator, or with a spreadsheet, if too complex for analytic solution).

We could proceed to add in the effect of activity, but our work above indicates that in fact, the basicity of  $F^-$  is (just barely) weak enough to be negligible with respect to the solubility of  $BaF_2$  – at least in 0.10 M NaF. (The result obtained above is, within sig figs, the same one you would get by solving the much simpler scenario in which you ignore activity coefficients and the basicity of  $F^-$ .)

**New PS 6 page: This new sheet has all the PS6 problems on it – so you only need to keep the excerpt from Harris from the original handout; this is now the complete problem statement, it has ALL of the problems from PS 6 on it.**

Remember to take your AA measurements this week, if you haven't already done so!