

Chapter 20. Cracolice, 2/e. Chemistry X11.

This is the last “chapter handout”.

We will discuss Ch 20 in class 13 (the last class before the final). We probably won't finish it. If time is short and/or this is new to you, emphasize Sect 1-6.

This is an extremely important chapter. The first sections discuss factors that affect how fast a reaction occurs. This is discussed in terms of “effective” collisions: collisions with enough energy to allow reaction. Focus on understanding Fig 20.2, and its implications. End-of-chapter questions 1-12 will help you with reaction rates and collision theory.

We have mainly discussed chemical reactions as if they always went “to the right” (in the direction of the usual arrow), with all of the reactant (or at least, of the limiting reactant; Sect 9.6) converted to product. However, that is not always so. Some reactions can go in both directions. As the reaction proceeds to the right, it slows down and the rate of the reverse reaction increases. Finally, an equilibrium is reached, in which the forward and reverse reactions proceed at the same rate. Thus there appears to be no further reaction. In fact, it is a dynamic equilibrium.

Recall earlier dynamic equilibria: vapor pressure, in Sect 15.4; saturated solutions, Sect 16.3; acid-base reactions (including ionization of water), Ch 18; redox, Ch 19.

Le Chatelier's principle (LCP; Sect 20.6) describes qualitatively how reversible reactions behave. Questions #13-20 are good practice with LCP; you should be able to do most of these. (Even if you get the hang of LCP, you will sometimes find a particular question that doesn't seem to work. Distinguish such an occasional specific problem from not understanding LCP.)

We can also deal with equilibria quantitatively. This is important if you are going on in chemistry; time will permit us only a brief introduction. However, recall K_w (Sect 18.8); it is a real example of an equilibrium constant. Sect 7 shows you how to write an equilibrium expression (“K expression”). Your first goal is to get the general pattern, and to see what it means (Sect 8). Then, remember to omit (l) and (s) chemicals. We will probably do only a few K calculations, Sect 9.

Further reading

V B E Thomsen, Le Chatelier's principle in the sciences. *J Chem Educ* 77:173, 2/00. Analogies to LCP in other fields, including physics, geology, biology, and economics. Some of the analogies are stretched, but in a sense that is the point... discussing how a possible analogy both does and does not fit helps reveal the underlying issues.

J Van Houten, Nobel centennial essays - A century of chemical dynamics traced through the Nobel prizes. 1909: William Ostwald. *J Chem Educ* 79:146, 2/02. Part of a series, reviewing some of the Chemistry Nobelists.

E A Davidson & I A Janssens, Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature* 440:165, 3/9/06. Review. A stretch of the Ch 20 ideas, to a bigger -- and very topical -- application. Their abstract: "Significantly more carbon is stored in the world's soils—including peatlands, wetlands and permafrost—than is present in the atmosphere. Disagreement exists, however, regarding the effects of climate change on global soil carbon stocks. If carbon stored belowground is transferred to the atmosphere by a warming-induced acceleration of its decomposition, a positive feedback to climate change would occur. Conversely, if increases of plant-derived carbon inputs to soils exceed increases in decomposition, the feedback would be negative. Despite much research, a consensus has not yet emerged on the temperature sensitivity of soil carbon decomposition. Unravelling the feedback effect is particularly difficult, because the diverse soil organic compounds exhibit a wide range of kinetic properties, which determine the intrinsic temperature sensitivity of their decomposition. Moreover, several environmental constraints obscure the intrinsic temperature sensitivity of substrate decomposition, causing lower observed 'apparent' temperature sensitivity, and these constraints may, themselves, be sensitive to climate."

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

Shakespeare and Thermodynamics: Dam the Second Law! The Human Importance of Activation Energies.