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eco-chem

Questions

Q158. Apply LeChatelier's principle, if appropriate, to predicting further change under the following conditions: (a) a freeway bypasses a city, (b) a government prints "unbacked" money, (c) infant mortality falls in a society, (d) a computer begins to check income tax returns against stock dividend checks, (e) a new anti-viral drug is introduced. In how many of these instances did the system approximate dynamic equilibrium (in the chemical sense) before the change was made? Comment.

Q159. The hydrolysis of urea at 100°C has a rate constant of 4.2×10^{-5} sec^{-1}. When catalyzed by the enzyme urease (5.1×10^{-10} *M*) at *p*H 8.0 and 20.8°C the first order rate constant is 3×10^4 sec^{-1}. The two values of $\Delta H\ddagger$ (activation energies) are 32.1 and 10.5 kcal/mole, respectively. Calculate the lowering of the free energy of activation caused by urease. Discuss the relative effects on activation energy and activation entropy due to the enzyme. [Shaw, W. H. R., and Walker, D. G., *J. Amer. Chem. Soc.*, **80**, 5337 (1958); Wall, M. C., and Laidler, K. J., *Arch. Biochem. Biophys.*, **43**, 299 (1953).]

Q160. Alpine lakes leave residues of 100–200 mg/l when evaporated but Scandinavian lakes often leave less than 50 mg/l. Discuss this in terms of chemicals present.

Answers

A158. LeChatelier's Principle may be stated: A dynamic equilibrium responds to any change by shifting in such a way as to minimize the effect of the change.

Dynamic equilibria involve mechanisms in each step of which identically opposite reactions occur at the same rate so no net change occurs and there are no net outputs or inputs. A steady state also has no net change but each mechanistic step proceeds only in one direction and all are at the same rate with a net input exactly balancing a net output for the whole system. (a) The traffic in and around a city approximates dynamic equilibria of cars and people, and freeways disturb the total system about as LeChatelier's Principle predicts. The increased freedom of traffic flow leads to an increase in traffic. Freeways through unsettled areas lead to population of these areas. In general, the problems the freeway was intended to solve recur once the freeway is built unless planned efforts are made to prevent the recurrence, such as zoning, tolls, and other restrictions. (b) Money flow often approximates a dynamic equilibrium for which the economic law of supply and demand serves as an example of LeChatelier's Principle. If the supply of money is increased, by printing more to make money more available, prices tend to rise to "use up" the new money, and vice versa. (c) Some societies are said to have equilibrium populations if they are increasing at a rate of no more than 1% annually but, actually, populations cannot come to dynamic equilibrium. Steady states are possible in which babies are born at essentially the same rate adults die. Thus, there is no reason to expect LeChatelier's Principle to apply. But it may shed insights even into steady states, and it is true that if infant mortality rates fall, and there are no other large factors changing, then before long adult mortality rates must rise (not much different from a dynamic equilibrium). (d) Flow of knowledge can approximate a dynamic equilibrium. When information is merely stored on paper subject to human scrutiny there is only a small likelihood that errors and misrepresentations will be found and the equilibrium state involves little feedback of information to the taxpayer and, perhaps, little information from the potential taxpayer to the tax collector. Addition of more revenue agents or of a computer increases the reverse flow which, in turn, increases the flow of information on dividend checks to the computer. But the analogy is not as good as in a) or b). One might argue, of course, that putting in the computer leads to the invention of new ways to cheat and a new "equilibrium." (e) Infections are hard to class as dynamic equilibria though often they are so described. It's a little hard to see what the equal and opposite rates are in the mechanisms of viral contagion. Thus, a good anti-viral drug (like Salk polio vaccine) can almost eliminate the disease. On the other hand, anti-viral drugs may assist the establishment of drug-resistant viral strains, a process reminiscent (if not directly analogous to) LeChatelier's Principle.

A159.

$$k_1 = \frac{kT}{h} e^{\Delta S^{*}/R} e^{-\Delta H^{*}/RT} = \frac{kT}{h} e^{-\Delta G^{*}/RT},$$

$$\Delta G^{*} = \Delta H^{*} - T\Delta S^{*}$$

Assume $\Delta H\ddagger$ and $\Delta S\ddagger$ are independent of *T*. Values of *G*, *H*, and *S* are in kcal, mole, and °K in appropriate combinations.

	k_1	kT/h	$e^{-\Delta G\ddagger/RT}$	$\Delta G\ddagger$	$\Delta H\ddagger$	$T\Delta S\ddagger$	$\Delta S\ddagger$
For the uncatalyzed reaction	4.2×10^{-5}	7.76×10^{14}	5.41×10^{-20}	33.0	32.1	−0.9	−0.00242
For the catalyzed reaction	3.1×10^{4}	6.11×10^{14}	5.08×10^{-11}	13.9	10.5	−3.4	−0.0115

The decrease in $\Delta G\ddagger$, 19.1 kcal/mole, is made up of a decrease of 21.6 kcal/mole in $\Delta H\ddagger$, and a decrease of 9.1 cal/Wmole K) in $\Delta S\ddagger$. The decrease in $\Delta S\ddagger$ actually tends to slow the catalyzed compared to the uncatalyzed reaction, but the decrease in $\Delta H\ddagger$ leads to a very large decrease in $\Delta G\ddagger$ and a large increase in the rate. Enzyme reactions almost always have a negative $\Delta S\ddagger$.

A160. Clearly the concentration of dissolved minerals is higher in Switzerland than in Scandinavia. The two most common types of rock are silicates and carbonates with the latter much more soluble in water, especially if the *p*H is low as may be true if decaying organic matter is contacted by the run off water. Swiss water is clearly more apt to have such contact than the more northern waters, due to the longer growing seasons and higher timber line. In addition, Scandinavian rocks are more preponderantly old silicates whereas the younger alps contain much more carbonate thrust up from old ocean beds by "recent" mountain building.