More Tutorial at www.LittleDumbDoctor.Com

1) W. A. Noyes studied the kinetics of the aqueous-phase oxidation-reduction reaction

$$2\ Fe^{+3}(aq)\ +\ Sn^{+2}(aq)\ \rightarrow\ 2\ Fe^{+2}(aq)\ +\ Sn^{+4}(aq)$$

and determined the following rate law in the presence of a high concentration of Fe^{+2}

$$\text{Rate} = k[Fe^{+3}]^2[Sn^{+2}]/[Fe^{+2}] \quad (1)$$

The following mechanism has been proposed for the reaction:

$$Fe^{+3}\ +\ Sn^{+2}\ \underset{-1}{\overset{1}{\leftrightarrow}}\ Fe^{+2}\ +\ Sn^{+3}$$

$$Fe^{+3}\ +\ Sn^{+3}\ \overset{2}{\rightarrow}\ Fe^{+2}\ +\ Sn^{+4}$$

a) Derive an empirical rate law for the reaction and show that it simplifies to the result reported by Noyes, i.e. equation (1).

Rate = d[product]/dt = $d[Sn^{+4}]/dt = k_2[Sn^{+3}][Fe^{+3}]$ (1)
The algebra in this problem is much simpler if one focuses on the products.
Under steady state conditions, Rate = $(1/1)d[Sn^{+4}]/dt = (-1/2)[Fe^{+3}]/dt$

We require the concentration of the intermediate Sn^{+3}. To this end, apply the steady-state approximation to this species.

$d[Sn^{+3}]/dt = k_1[Sn^{+2}][Fe^{+2}] - k_{-1}[Sn^{+3}][Fe^{+2}] - k_2[Fe^{+3}][Fe^{+3}] \approx 0$ (2)

Hence, $[Sn^{+3}] = k_1[Fe^{+3}][Sn^{+2}]/(k_{-1}[Fe^{+2}] + k_2[Fe^{+3}])$ (3)

Substituting (2) into (1), one obtains Rate = $k_1[Fe^{+3}]^2[Sn^{+2}]/(k_{-1}[Fe^{+2}] + k_2[Fe^{+3}])$
In the presence of a large concentration of Fe^{+2}, the Fe^{+2} term in the denominator dominates and the rate law simplifies to

Rate = $(k_1k_2/k_{-1})[Fe^{+3}]^2[Sn^{+2}]/[Fe^{+2}]$ which is the observed result.

b) Suppose that the value of the microscopic rate constant k_2 is required. What other information (be specific) could be combined with the value of the empirical rate constant k to yield a value of k_2?

$k = k(\text{empirical}) = k_1k_2/k_{-1}$. One can obtain the value of k_2 by combining k with the value of the equilibrium constant for the first step $K_1 = k_1/k_{-1}$.

c) Show that the empirical rate law, i.e. equation (1), is consistent with the nature of the activated complex.

One reaches the activated complex in the second, rate-determining bimolecular step by combining Sn^{+3} and Fe^{+3}. Hence the activated complex will have the molecular formula $FeSn^{+6}$ (charges and mass add).

Using the exponents in the rate law one obtains:
Stoichiometry: (2 x Fe) + (1 x Sn) + (-1 x Fe) = FeSn
Charge: (2 x +3) + (1 x +2) + (-1 x +2) = +6

d) If one plans to repeat the work of Noyes, which experimental variables must be controlled if one wishes to collect interpretable kinetic data?

Temperature (rate constants are T dependent), ionic strengths (activity coefficients of ions deviate from unity), and pH (iron species can precipitate as hydroxides at high pH)

e) Speculate on the value of the standard entropy of activation, $\Delta S^{\dagger}$, for the second forward step in the mechanism.

In the slow step, two monatomic species combine to form a bimolecular activated complex. The entropy of activation is negative. The net entropy change for the reaction (not what was requested) is close to zero.

2) A. Farkas and L Farkas showed that the bimolecular rate constant for the elementary gas-phase reaction $H_2(g) + H(g) \rightarrow H(g) + H_2(g)$ has the following form:

$$k = BT^{0.5}\exp(-C/RT) \quad (C = 23000 \text{ J/mole}) \quad (2)$$

a) Provide a simple explanation for the $T^{0.5}$ term. (One model will be the key.)

In the collisional model, the rate constant is proportional to the average relative speed which in turn is proportional to the square root of the temperature.

b) Derive an expression for the standard enthalpy of activation, $\Delta H^{\dagger}$.

N.B., the enthalpy of activation is a slope!

$\Delta H^{\dagger} = -R[d\ln(k/T)/d1/T)]$

$\ln(k/T) = \ln B - 0.5\ln T - C/RT$

$d\ln(k/T)/(1/T) = 0 - 0.5[d\ln T/d1/T)] - C/R$ and $d\ln T/d(1/T) = -T$

Hence, $\Delta H^{\dagger} = C = RT/2$

c) Suppose that D_2 is used instead of H_2. Will the rate constant k increase, decrease, or remain the same as a result of the substitution.

Kinematics make a small contribution to k. The dominant effect comes from the stability of the hydrogen molecule. The dissociation of the more massive D_2 requires more energy than the lighter H_2. Hence, the rate constant for the reaction with D_2 will be smaller than that for H_2. This is an example of the primary kinetic isotope effect.

3) At 25°C how far will a globular protein with a radius of 250 Å diffuse in 2.0 s? The solvent is water with a viscosity of 0.000900 $Kgm^{-1}s^{-1}$.

Probability theory plays a role in this problem because diffusion is a random-walk problem. We can only calculate odds that a molecule will travel a specified distance. A relevant measure is σ, the distance traveled by 68% of the protein molecules.

In three dimensions, $\sigma = [6Dt]^{0.5}$.

Using the Stokes equation, $D = k_BT/(6\pi\eta r)$ or
$(1.38 \times 10^{-23}$ J/K-molec)(298 K)/[6π(0.000900 Kg/m-s)$(250 \times 10^{-10}$ m)]
$= 250 \times 10^{-10}$ m^2/s

Hence, $\sigma = [(6)(250 \times 10^{-10}$ m)(2.0 s)]0.5 = 1.1×10^{-8} m.

WES, 19 April 2004