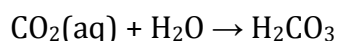


Chemistry for Earth Sciences

Practical 6: Kinetics of Geochemical processes (WORKED SOLUTIONS)

1. The hydration of dissolved CO₂ (i.e., CO₂(aq) + H₂O = H₂CO₃) has an equilibrium constant of 1.7 x 10⁻³. The rate of the forward reaction



follows the first-order rate law:

$$-\frac{d[\text{CO}_2(\text{aq})]}{dt} = k_f[\text{CO}_2(\text{aq})]$$

k_f has been determined to be 0.039 sec⁻¹.

a) What is the rate law and rate constant k_r for the reverse reaction?

SOLUTION:

$$-\frac{d[\text{H}_2\text{CO}_3]}{dt} = k_r[\text{H}_2\text{CO}_3]$$

b) If 0.001 mole of CO₂ is added to 1kg of H₂O, how long will it take to consume 99% of the CO₂ if we neglect the reverse reaction (i.e., if H₂CO₃ is constantly removed from the system)? Because this reaction is not instantaneous, organisms need an enzyme (carbonic acid anhydrase) to facilitate it in cellular processes.

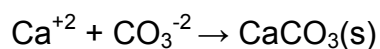
SOLUTION:

If we integrate the rate law for the forward reaction, we get

$$\ln\left(\frac{[\text{CO}_2]_t}{[\text{CO}_2]_0}\right) = -kt$$

Our initial condition $[\text{CO}_2]_0 = 0.001$ moles; our final condition, $[\text{CO}_2]_t = 0.99[\text{CO}_2]_0$. So, $\ln(0.99) = -kt = -0.039t$ or $t = 0.25$ seconds.

2. (a) Assuming that the precipitation of calcite from aqueous solution occurs only through the reaction:

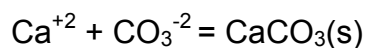


and that this reaction is *elementary*, write an equation for the rate of calcite precipitation.

SOLUTION:

$$\frac{d[\text{Ca}]}{dt} = -k_f[\text{Ca}^{+2}][\text{CO}_3^{-2}]$$

(b) Assuming that the reaction above is reversible, i.e.:



and still assuming that it is *elementary*, write an equation for the dependence of *net* rate of calcite precipitation on concentration and free energy change of reaction.

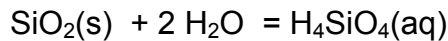
SOLUTION:

$$\text{Rate}_{net} = k_f[\text{Ca}^{+2}][\text{CO}_3^{-2}] - k_r$$

From transition state theory, we have that

$$\begin{aligned} \text{Rate}_{net} &= \text{Rate}_{forward} (1 - e^{-\Delta G/RT}) \\ &= k_f[\text{Ca}^{+2}][\text{CO}_3^{-2}](1 - e^{-\Delta G/RT}) \end{aligned}$$

3. The dissolution/precipitation of quartz (SiO_2) occurs by the reaction



The net rate law for this reaction is (Rimstidt and Barnes, 1980):

$$\frac{d[\text{H}_4\text{SiO}_4]}{dt} = A(k_f - k_r[\text{H}_4\text{SiO}_4])$$

Where k_f is the rate constant for the dissolution reaction and k_r is the rate constant for the precipitation reaction. A is the surface area (m^2) of quartz per kg of water.

a) Show that the equilibrium constant for this reaction is

$$K = \frac{k_f}{k_r}$$

SOLUTION:

At equilibrium, the net rate is zero ($[\text{H}_4\text{SiO}_4]$ is constant and $= K$). Hence,

$$\frac{d[\text{H}_4\text{SiO}_4]}{dt} = A(k_f - k_r[\text{H}_4\text{SiO}_4]) = 0$$

$$k_f = k_r[\text{H}_4\text{SiO}_4]$$

$$[\text{H}_4\text{SiO}_4] = K = \frac{k_f}{k_r}$$

b) The rate constants have a temperature dependence of

$$\log k_f = 1.174 - 2.028 \times 10^{-3} T - 4158 / T$$

$$\log k_r = -0.707 - 2598 / T$$

where T is in Kelvin. Work out the approximate activation energies for the forward and reverse reactions and the free energy difference between quartz and dissolved H_4SiO_4 (1m).

SOLUTION:

From transition state theory,

$$k = \frac{k_B T}{h} e^{-\Delta G^\ddagger / RT}$$

Where ΔG^\ddagger is the activation energy. Hence,

$$\log k = \log\left(\frac{k_B T}{h}\right) + \frac{-\Delta G^\ddagger}{2.303RT}$$

So, to a good approximation, the activation energy for the forward reaction is $4158 \times 2.303R = 79.6$ kJ/mole and the activation energy for the reverse reaction is 49.7 kJ/mole.

c) Show that we can rewrite the rate law as:

$$\frac{d[H_4SiO_4]}{dt} = Ak_f\left(1 - \frac{Q}{K}\right)$$

where Q is the reaction quotient (= $[H_4SiO_4]$ in this case..).

SOLUTION:

$$\frac{d[H_4SiO_4]}{dt} = A(k_f - k_r[H_4SiO_4])$$

Since

$$K = \frac{k_f}{k_r}$$

$$[H_4SiO_4] = Q$$

It follows that

$$\frac{d[H_4SiO_4]}{dt} = Ak_f \left(1 - \frac{Q}{K}\right)$$

d) Integrate the rate law to work out Q ($= [H_4SiO_4]$) as a function of time. If the surface area of quartz is fixed at $1 \text{ cm}^2/\text{kg}$ water, how long will it take a solution to be 50% saturated in quartz (i.e., $Q = 0.5 K$) at $T = 25^\circ \text{C}$ and 350°C .

SOLUTION:

To integrate the rate law, we use a "change of variable" technique: we set

$$X = \left(1 - \frac{Q}{K}\right)$$

$$dX = -\frac{1}{K} dQ$$

$$\frac{-KdX}{dt} = Ak_f X$$

$$\frac{dX}{X} = \frac{-Ak_f}{K} dt$$

$$\ln\left(\frac{X}{X_0}\right) = \frac{-Ak_f}{K} t$$

Since $X = 1 - Q/K$, when X_0 is 1 and when $Q = 0.5 K$, $X = .5$ so

$$\ln(0.5) = \frac{-Ak_f}{K} t$$

$$t = -\ln(0.5) * K / (Ak_f)$$