Key for Thermodynamics and Kinetics

Task One. For a reaction with the general form $X \rightleftharpoons Y$, the rate of the forward reaction, $R_f = k_f[X]$, and the rate of the reverse reaction, $R_r = k_r[Y]$, are equal. Setting the rates equal to each other gives

$$k_f[X] = k_r[Y]$$

Solving for the equilibrium constant shows that

$$K_{eq} = \frac{[Y]}{[X]} = \frac{k_f}{k_r}$$

Substituting into this equation the values for $K_{\mathrm{A \to B}}$ for k_f and $K_{\mathrm{B \to A}}$ for k_r yields the equilibrium constant K_{AB}

$$K_{eq} = \frac{0.1000}{0.0667} = 1.499$$

showing that the equilibrium and kinetic information are self-consistent. The same holds true for the reaction $\mathrm{A} \rightleftharpoons \mathrm{C}$.

Task 2. Based on its larger K_{eq} we expect citric acid is the favored product.

Task 3. To find the equilibrium composition use an ICE table starting with 100 units of A and 0 units of C. At equilibrium you should find that the mixture contains 95.83 units of C and 4.17 units of A.

Task 4. Here we do not need to use an ICE table. Instead we know that K_{AB} is 1.50 and that at equilibrium we have 4.17 units of A; thus, at equilibrium we have 6.28 units of B. Note that we started with 100 units of A and now have more than 100 units of A, B and C. This apparent violation of the conservation of mass is an artifact of the approach to finding the equilibrium distributions. We take care of this in the next task by finding the relative abundance of each species.

Task 5. There are 106.28 total units, of which approximately 90% are C, 4% are A and 6% are B.

Task 6. The answers here will vary. All answers should, however, start with 100 units of A and 0 units of B and C at time $t = 0$ and end with 90 units of C, 4 units of A and 6 units of C at the time where equilibrium is reached. After equilibrium the relative numbers of units should remain constant. How you show the reaction moving from its beginning to equilibrium depends upon your insight. The most common sketch shows the concentration of A smoothly decreasing and the concentrations for B and C smoothly increasing. The correct sketch is shown on the reverse of this page.

Task 7. At the beginning of the reaction both B and C accumulate at equal rates because the rate constants for $\mathrm{A} \to \mathrm{B}$ and $\mathrm{A} \to \mathrm{C}$ are identical. Thus, at the beginning of the reaction the relative abundance of B and C are controlled by kinetics. Because the rate constant for $\mathrm{B} \to \mathrm{A}$ is much larger than that for $\mathrm{C} \to \mathrm{A}$, a unit of B is more likely to change back to an A and then to a C, than a unit of C is to change to an A and then to a B. Over time the kinetics brings the system to its equilibrium position. Chemists frequently take advantage of this in synthetic work when the desired product is favored by kinetics but not by thermodynamics. As the reaction proceeds, the desired product is removed before it has a chance to convert to the less desired thermodynamic product.

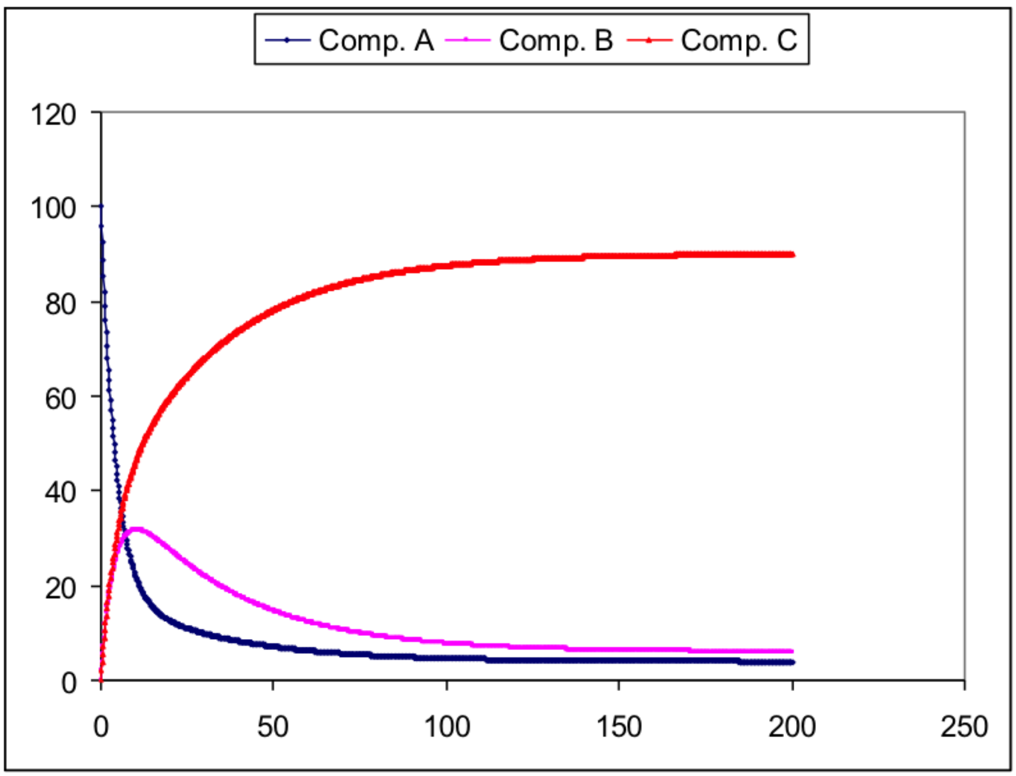

Figure 1: Concentration vs. time curves for A: cis-aconitic acid; B: isocitric acid; C: citric acid