3. (a) (i) Br^- is first order because when the $[\mathrm{Br}^-]$ doubles, while $[\mathrm{BrO_3}^-]$ and $[\mathrm{H}^+]$ remain constant (as in Experiments 1 and 2), the rate of the reaction doubles. This shows $[\mathrm{Br}^-]$ to the first power is directly proportional to rate of the reaction. So, the reaction is first order with respect to $[\mathrm{Br}^-]$.

(ii) $\mathrm{BrO_3}^-$ is first order because when the $[\mathrm{BrO_3}^-]$ increases by a factor of 1.5, while $[\mathrm{Br}^-]$ and $[\mathrm{H}^+]$ remain constant (as in Experiments 1 and 3), the rate of the reaction increases by a factor of 1.5. This shows $[\mathrm{BrO_3}^-]$ to the first power is directly proportional to rate of the reaction. So, the reaction is first order with respect to $[\mathrm{BrO_3}^-]$.

(iii) H^+ is second order because when the $[\mathrm{H}^+]$ doubles the rate of the reaction quadruples. Experiments 3 and 4 best illustrate this relationship. In these two experiments $[\mathrm{Br}^-]$ remains constant while $[\mathrm{BrO_3}^-]$ and $[\mathrm{H}^+]$ both double causing the rate of the reaction to increase by a factor of eight. Since it was shown above in 3 (a) (ii) that $[\mathrm{BrO_3}^-]$ is first order, doubling $[\mathrm{BrO_3}^-]$ will cause the rate to double; therefore, doubling the $[\mathrm{H}^+]$ was responsible for the remaining increase in the rate of the reaction by a factor of four. This shows $[\mathrm{H}^+]$ to the second power is directly proportional to rate of the reaction. So, the reaction is second order with respect to $[\mathrm{H}^+]$.

(b) Rate = $k[\mathrm{Br}^-][\mathrm{BrO_3}^-][\mathrm{H}^+]^2$

(c) Any of the four experiments can be chosen. For example, Experiment 1 shows the concentrations of each of reactants and the rate of the reaction. These values are substituted into the rate law in 3 (b) above and solve for the rate constant, k.

Rate = $k[\mathrm{Br}^-][\mathrm{BrO_3}^-][\mathrm{H}^+]^2$

$$2.5 \times 10^{-4}\ \frac{\text{mole}}{\text{L}\cdot\text{s}} = k\left(0.00100\ \frac{\text{mole}}{\text{L}}\right)\left(0.00500\ \frac{\text{mole}}{\text{L}}\right)\left(0.100\ \frac{\text{mole}}{\text{L}}\right)^2$$

$$\boxed{k = 5000\ \frac{\text{L}^3}{\text{mol}^3\cdot\text{s}}}$$

(d) The first half reaction must be reversed and multiplied by $\frac{5}{2}$ so the coefficients will match those in the overall reaction producing the following table:

Half-reaction	E° (V)
$5\mathrm{Br}^-(aq) \rightarrow \frac{5}{2}\,\mathrm{Br}^2(l) + 5\,e^-$	-1.065
$\mathrm{BrO_3}^-(aq) + 6\,\mathrm{H}^+(aq) + 5\,e^- \rightarrow \frac{1}{2}\,\mathrm{Br_2}(l) + 3\,\mathrm{H_2O}(l)$	+1.52

So, the net cell potential would be -1.065 V + 1.52 V = $\boxed{0.46\ \text{V} = E^\circ}$

(e) The total number of electrons would be 5 moles (from the balanced half-reactions) times Avogadro's number of electrons in each mole.

$$(5\ \text{moles of electrons})\cdot\left(6.02 \times 10^{23}\ \text{electrons}/\text{mole}\right) = 3.01 \times 10^{24}\ \text{electrons}$$

$$\boxed{\text{total number of elecrons transferred} = 3.01 \times 10^{24}\ \text{electrons}}$$

7. (a.) $O_3 + O \rightarrow O_2$

(b) Cl is the catalyst because it is used in step 1 of the proposed mechanism, but an equal quantity of Cl is produced in step 2 of this mechanism. Therefore, in the overall reaction it used but not consumed-this is the definition of a catalyst.

(c) ClO is the intermediate because it is produced in step 1 of the proposed mechanism, but an equal quantity of ClO is consumed in step 2 of this mechanism. When O_3 collides with Cl one of the O-O bonds in O_3 breaks as a Cl-O bond forms between the Cl and the O atom that broke away from the O_3 molecule. ClO forms temporarily but when another O atom collides with ClO the Cl-O bond breaks as an O-O bond forms between this new O atom and the O atom from the broken Cl-O bond. So, ClO forms temporarily but then reacts with another species to produce a product.

(d) (i) 2 (1 from the exponent of $[O_3\}$ and 1 from the exponent of [Cl])

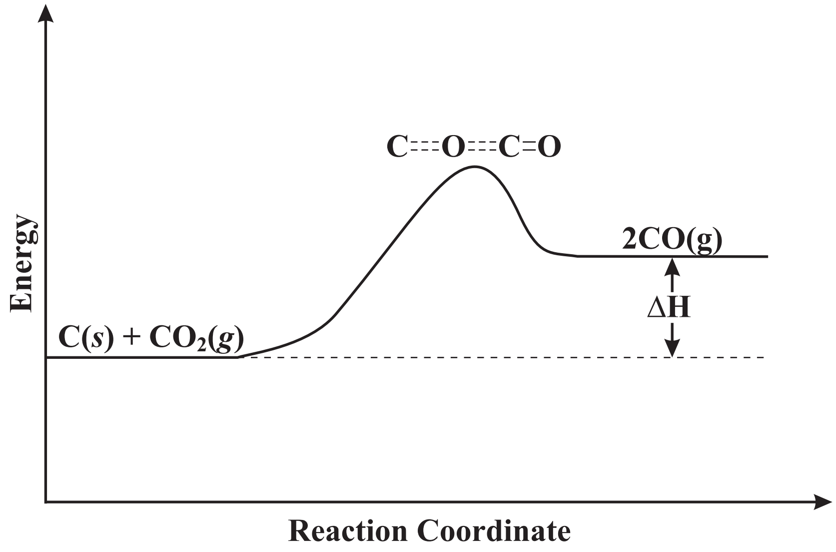
(ii) $\frac{\text{L}}{\text{mol}\cdot\text{s}} \left(\frac{\text{Liters}}{\text{mole}\cdot\text{seconds}}\right)$

(iii) The first step is the rate-determing step because the rate law of this step, which can betermined from its molecularity (i.e. the exponents can be determined from the coefficients of the balanced equation-it does not have to be determined by experiment) is the rate law of the overall reaction. This match of the rate law for the overall reaction with a particular step is true only for a rate-determining step. Therefore, the first step is the rate-determing step.

8. (a) The sign of ΔS for the reaction will be positive because entropy is increasing toward the products due to an increase in the number of gas molecules (from 1 to 2) which increases the positional probability, which, by definition, is an increase in entropy.

(b) The sign of ΔH for the reation is positive because an increase in temperature (by adding energy) shifts the equilibrium to the right. This is true for an endothermic reaction, which has a positive ΔH), because in an endothermic reaction, energy is treated as a reactant (it is consumed in the reaction) and adding energy would, then, shift the equilibrium to the right according to Le Chatelier's Principle which says any stress exerted on an equilibrium condition will cause the reaction that was at equilibrium to shift so as to alleviate that stress. In this case, the stress is cuased by raising the temperature, or adding energy. Since energy is treated as a reactant in an endothermic reaction, the equilibrium will shift to the right (the products) to poroduce more CO(*g*) which alleviates the increase in the reactant energy by consuming the energy as the reaction proceeds to the right.

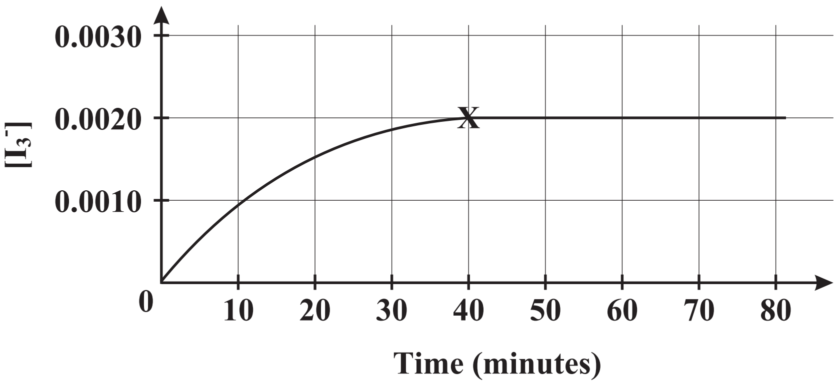
(c)



(d) Doubling the amount of C(*s*) would have no effect on the percent of CO in the equilibrium because C(*s*) is a pure solid and the concentration of a pure solid (or pure liquid) cannot change because doubling its amount also doubles its volume so its concentration remains the same.

6. (a) This is an oxidation-reduction reaction iodine is oxidized from -1 to $-\frac{1}{3}$ while sulfur is reduced from +7 to +3. Another substance that can convert I^-(aq) to I_3^-(aq) is $Se_2O_8^{2-}$.

(b)



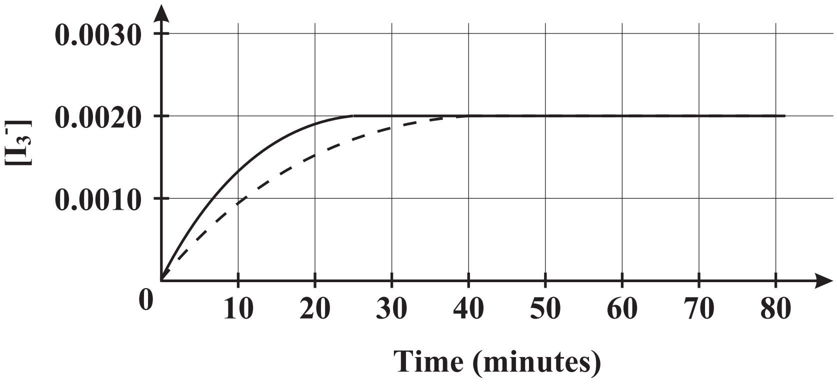
(i) The X should be placed at 40 minutes because after this time the concetration of I_3^-(aq) does not change indicating the reaction is in equilibrium.

(ii) Draw a tangent line to the curve that touches the graph at 20 minutes. Take the slope of this tangent line. The slope is the instantaneous rate of formation of I_3^-(aq).

(c) Double the initial concentration of I^-(aq) to 0.0240 M while keeping the concentration of $S_2O_8^{2-}$(aq) a constant and determine the initial rate of the reaction. If the rate compare this rate to the rate from the original experiement. Use the equation $\left(\frac{Rate_2}{Rate_1}\right)^m = \left(\frac{Concentration_2}{Concentration_1}\right)$ and the data from these experiments to determine the exponent, m. This exponent, m, is the order of the reaction with respect to I^-(aq). To determine the order of the reaction with respect to $S_2O_8^{2-}$ (aq), double the concentration of $S_2O_8^{2-}$(aq) from original experiment to 0.0080 M while keeping the concentration of I^-(aq) a constant 0.0120 M (the same as the original experiment) and determine the initial rate of the reaction. If the rate compare this rate to the rate from the original experiement. Use the equation $\left(\frac{Rate_3}{Rate_1}\right)^p = \left(\frac{Concentration_3}{Concentration_1}\right)$ and the data from these experiments to determine the exponent, p. This exponent, p, is the order of the reaction with respect to $S_2O_8^{2-}$(aq)

(d) If the order of the reaction is zeroth order, a plot of the concentration of the reactant versus time could be plotted (yielding a straight line) and the slope of this line would equal -k. If the order of the reaction is first order, a plot of the natural log of the concentration of the reactant versus time could be plotted (yielding a straight line) and the slope of this line would equal -k. If the order of the reaction is second order, a plot of one divided by the concentration of the reactant versus time could be plotted (yielding a straight line) and the slope of this line would equal k.

(e) It would reach equilibrium quicker at 35 °C.



6. (a) $\Delta H° = \Sigma\Delta H_f^o \text{products} - \Sigma\Delta H_f^o \text{reactants}$

$$\Delta H° = \left[\Delta H_f^o(O_2) + \Delta H_f^o(NO_2)\right] - \left[\Delta H_f^o(O_3) + \Delta H_f^o(NO)\right]$$

$\Delta H°$ = (0 kJ/mol + 33 kJ/mol) - (143 kJ/mol + 90 kJ/mol)

$$\boxed{\Delta H° = -200 \text{ kJ}}$$

(b) $\Delta S°$ for the reaction will be zero because there is no increase in entropy (disorder). There are the same number of gas particles on the reactant side as the product side.

(c) $\Delta G° = \Delta H° - T\Delta S°$ Since $\Delta S°$ is zero and $\Delta H°$ is negative, $\Delta G°$ should be negative.

(d) Compare experiment number 3 to 1.

$$\left(\frac{[O_3]_3}{[O_3]_1}\right) = \left(\frac{Rate_3}{Rate_1}\right)^m$$

$$\left(\frac{0.0020M}{0.0010M}\right) = \left(\frac{2x}{x}\right)^m$$

$2 = 2^m$

$m = 1$

Compare experiment number 2 to 1.

$$\left(\frac{[NO]_2}{[NO]_1}\right) = \left(\frac{Rate_2}{Rate_1}\right)^n$$

$$\left(\frac{0.0020M}{0.0010M}\right) = \left(\frac{2x}{x}\right)^n$$

$2 = 2^n$

$n = 1$

$\text{Rate} = k[O_3]^m[NO]^n = k[O_3]^1[NO]^1$

$$\boxed{\text{Rate} = k[O_3][NO]}$$

(e) Step I is the rate-determining (the slowest step) since the rate law written from its molecularity matches the rate law determined from experimentation in part (c.) above.