1) We have the balanced equation and the rate law; we need to collect some thermochemical data.

\[
\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g) \quad \text{rate} = 0.515 \text{ L/(mol\cdot s)}[\text{NO}_2]^2
\]

\[\Delta H^\circ = 33.2 \quad -110.5 \quad 90.29 \quad -393.5 \quad \text{(all in kJ/mol).}\]

The thermochemical data lead to a \(\Delta H_{\text{rxn}} = (-393.5) + 90.29 - (33.2 + (-110.5)) = -225.91 \text{ kJ/mol.}\)

Given the concentration of NO\(_2\), we can get the initial rate: rate = \(0.515 \text{ L/(mol\cdot s)}(0.0275 \text{ M})^2 = 3.895 \times 10^{-4} \text{ mol/(L\cdot s)}\). Multiplying this by the \(\Delta H_{\text{rxn}}\) and then by the volume we have will give us the heat evolved per second by this reaction: \((3.895 \times 10^{-4} \text{ mol/(L\cdot s)})(-225.91 \text{ kJ/mol})(3.35 \text{ L}) = 0.295 \text{ kJ/s} = 295 \text{ J/s.}\)

2) Starting with \(PV = nRT\), we can divide by \(V\) to get: \(P_x = MRT\) (\(n/V\) is moles/volume or molar) or \(M = P_x RT\). If the rate law is:

\[-\Delta[\text{H}_2]/\Delta t = (1.10 \times 10^{-7} \text{ M}^{-2} \text{ s}^{-1})[\text{NO}]^2[\text{H}_2],\]

we can write this as:

\[-\Delta[\text{H}_2]/\Delta t = (1.10 \times 10^{-7} \text{ M}^{-2} \text{ s}^{-1})(P_{\text{NO}}/RT)^2(P_{\text{H}_2}/RT)\]

\[-\Delta[\text{NO}]/\Delta t = (2.20 \times 10^{-7} \text{ M}^{-2} \text{ s}^{-1})(P_{\text{NO}}/RT)^2(P_{\text{H}_2}/RT)\] [recall the stoichiometry and how to adjust for this stoichiometry.]

Making the necessary substitutions, we get: \((P_{\text{NO}} = 0.203 \text{ atm}; P_{\text{H}_2} = 0.453 \text{ atm})\)

\[-\Delta[\text{NO}]/\Delta t = (2.20 \times 10^{-7} \text{ M}^{-2} \text{ s}^{-1}) \left[\frac{0.203}{(0.08206)(1099)}\right]^2 \left[\frac{0.453}{(0.08206)(1099)}\right] = 5.60 \times 10^{-15} \text{ M/s.}\]

Multiplying by RT gives \(5.05 \times 10^{-13} \text{ atm/s}, which, when multiplied by 760 mm Hg/atm, gives \(3.84 \times 10^{-10} \text{ mm Hg/s.}\)

3) We have here a nice application of concentration-time dependence, using a first order reaction. We need to a) calculate a rate constant given our data; b) use this rate constant to calculate a concentration at some later time.

We know that we have a half-life of 9.0 minutes, so we can get the rate constant,

\[k = \frac{0.693}{9 \text{ min}} = 7.7 \times 10^{-2} \text{ min}^{-1}.\]
Now we can say that \([\text{Biac}]_t = 0.85[\text{Biac}]_0\), which allows us to simplify our expression \(\ln\left(\frac{[\text{Biac}]_t}{[\text{Biac}]_0}\right) = -0.077/\text{min}(t)\) to \(\ln(0.85) = -0.077t\), and solve for \(t\). Doing so gives us \(t = 2.11\) minutes.

4) Let \([\text{Acet}]\) represent acetone, \([\text{AcetH}^+]\) represent the protonated acetone, and \([\text{Acet}^*\text{H}^+]\) represent the \(\text{CH}_3\text{C(OH)=CH}_2\) species. Also let the first mechanistic step have rate constants \(k_1\) and \(k_{-1}\), the second have rate constant \(k_2\) and the third (and last) have constant \(k_3\). Then we can start as:

\[
\text{rate} = \text{rate}_2 = k_2[\text{AcetH}^+][\text{H}_2\text{O}].
\]

From this, we see that we need to determine an expression for \([\text{AcetH}^+]\), as it is a reaction intermediate (and possibly \([\text{H}_2\text{O}]\)). From the first, fast equilibrium we get:

\[
\text{rate}_1 = k_1[\text{Acet}][\text{H}_3\text{O}^+] = \text{rate}_{-1} = k_{-1}[\text{AcetH}^+][\text{H}_2\text{O}].
\]

Solving for \([\text{AcetH}^+]\)[\text{H}_2\text{O}] we get: \([\text{AcetH}^+]\)[\text{H}_2\text{O}] = \frac{k_1}{k_{-1}}[\text{Acet}][\text{H}_3\text{O}^+].\) Making the substitution into the proposed rate law, we get:

\[
\text{rate} = \text{rate}_2 = \frac{k_1k_2}{k_{-1}} [\text{Acet}][\text{H}_3\text{O}^+].
\]

which yields a perfectly acceptable rate law, since it contains only those species present in the balanced chemical equation. (Remember that catalysts may appear but do not have to appear in the rate law).