

HW 13 key

1. a) Our definition of rates has taken the form

$$v(t) = -\frac{1}{V} \frac{1}{\nu_A} \frac{dn_A}{dt} = -\frac{d[A]}{\nu_A dt}$$

We have assumed that volume remains constant, so the only influence on the concentration of A is from changes in moles, not changes in volume.

b) need a function in which [A] changes both as a function of n and V:

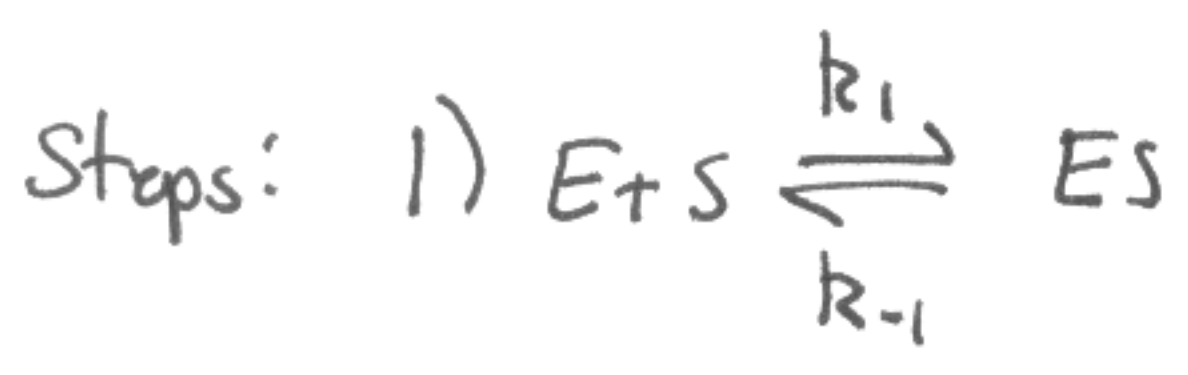
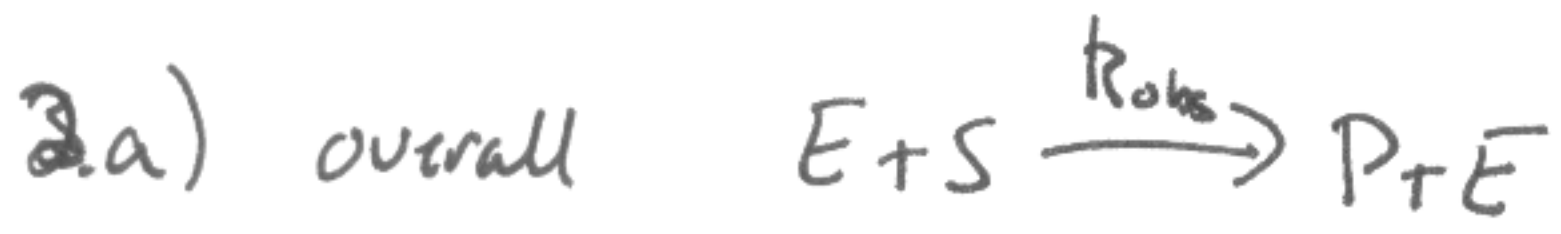
$$[A] = \frac{n}{V}$$

$$\frac{d[A]}{dn} = \frac{1}{V} ; \quad d[A] = \frac{dn}{V}$$

$$\frac{d[A]}{dV} = -\frac{1}{V^2} ; \quad d[A] = -\frac{1}{V^2} dV$$

$$d[A] = \frac{dn}{V} - \frac{dV}{V^2}$$

$$v(t) = -\frac{1}{\nu_A} \left(\frac{dn}{V} - \frac{dV}{V^2} \right) dt$$



$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] = 0 \quad (SSA)$$

$$\frac{d[P]}{dt} = k_2[ES]$$

Solve for [ES]: $[ES] = \frac{k_1[E][S]}{k_{-1} + k_2}$

$$\boxed{\frac{d[P]}{dt} = \frac{k_1 k_2 [E][S]}{k_{-1} + k_2}}$$

3. $v = k [Cr(H_2O)_4^{3+}]^m [SCN^-]^n$

compare expts. 1 and 3: $m = \frac{\ln \left(\frac{v_1(t)}{v_3(t)} \right)}{\ln \left(\frac{[Cr]_1}{[Cr]_3} \right)}$ ← entire Cr complex

$$m = \frac{\ln \left(\frac{2.11 \times 10^{-11} \text{ mol/Ls}}{2.84 \times 10^{-11} \text{ mol/Ls}} \right)}{\ln \left(\frac{1.21 \times 10^{-4} \text{ mol/L}}{1.66 \times 10^{-4} \text{ mol/L}} \right)} = 0.94 \approx 1$$

* rxn is 1st order in Cr.

3

We don't have a set of similar data for $[\text{SCN}^-]$, so we have to improvise. If we compare expts. 1 and 4, we see

that expt. 4 has 1.5x as much Cr as ~~expt. 1~~ expt. 1.

IF we had increased the ~~rate~~ $[\text{Cr}]$ by 1.5 and left $[\text{SCN}^-]$ constant, then the rxn rate would have increased by a factor of 1.5:

real expt 1:

$$[\text{Cr}] = 1.21 \times 10^{-4} \text{ mol/L}$$

$$[\text{SCN}^-] = 1.05 \times 10^{-5} \text{ mol/L}$$

$$v_1(t) = 2.11 \times 10^{-11} \text{ mol/Ls}$$

imaginary expt 1: (call 1*)

$$[\text{Cr}] = 1.83 \times 10^{-4} \text{ mol/L}$$

$$[\text{SCN}^-] = 1.05 \times 10^{-5} \text{ mol/L}$$

$$v_{1^*}(t) = 3.17 \times 10^{-11} \text{ mol/Ls}$$

so now we will use the data from expts 1* and 4:

$$n = \frac{\ln\left(\frac{v_{1^*}(t)}{v_4(t)}\right)}{\ln\left(\frac{[\text{SCN}^-]_1}{[\text{SCN}^-]_4}\right)} = \frac{\ln\left(\frac{3.17 \times 10^{-11} \text{ mol/Ls}}{9.44 \times 10^{-11} \text{ mol/Ls}}\right)}{\ln\left(\frac{1.05 \times 10^{-5} \text{ mol/L}}{3.11 \times 10^{-5} \text{ mol/L}}\right)}$$

$$n = 1.0121$$

$$\text{so } v(t) = k [\text{Cr}(\text{H}_2\text{O})_6^{3+}] [\text{SCN}^-]$$

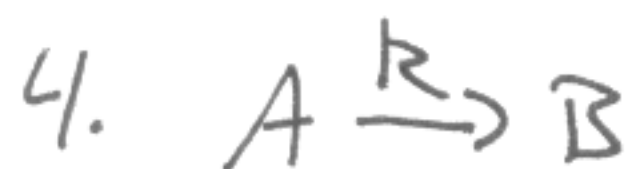
Still need to find k : use any set of data:

(4)

from expt 3:
$$k = \frac{v_3}{[\text{Cr}]_3 [\text{SCN}]_3} = \frac{2.82 \text{ mol/L s}}{(1.66 \times 10^{-4} \text{ mol/L})(1.02 \times 10^{-5} \frac{\text{mol}}{\text{L}})}$$

$$k = 0.017 \text{ L/mol s}$$

so full rate law:
$$v(t) = 0.017 \text{ L/mol s} [\text{Cr}(\text{H}_2\text{O})_6^{3+}] [\text{SCN}^-]$$



$$v(t) = -\frac{d[A]}{v_A dt} = k[A]$$

rearrange:
$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -v_A k \int_0^t dt$$

$$\ln\left(\frac{[A]}{[A]_0}\right) = -v_A k t$$

$$[A] = [A]_0 e^{-v_A k t}$$

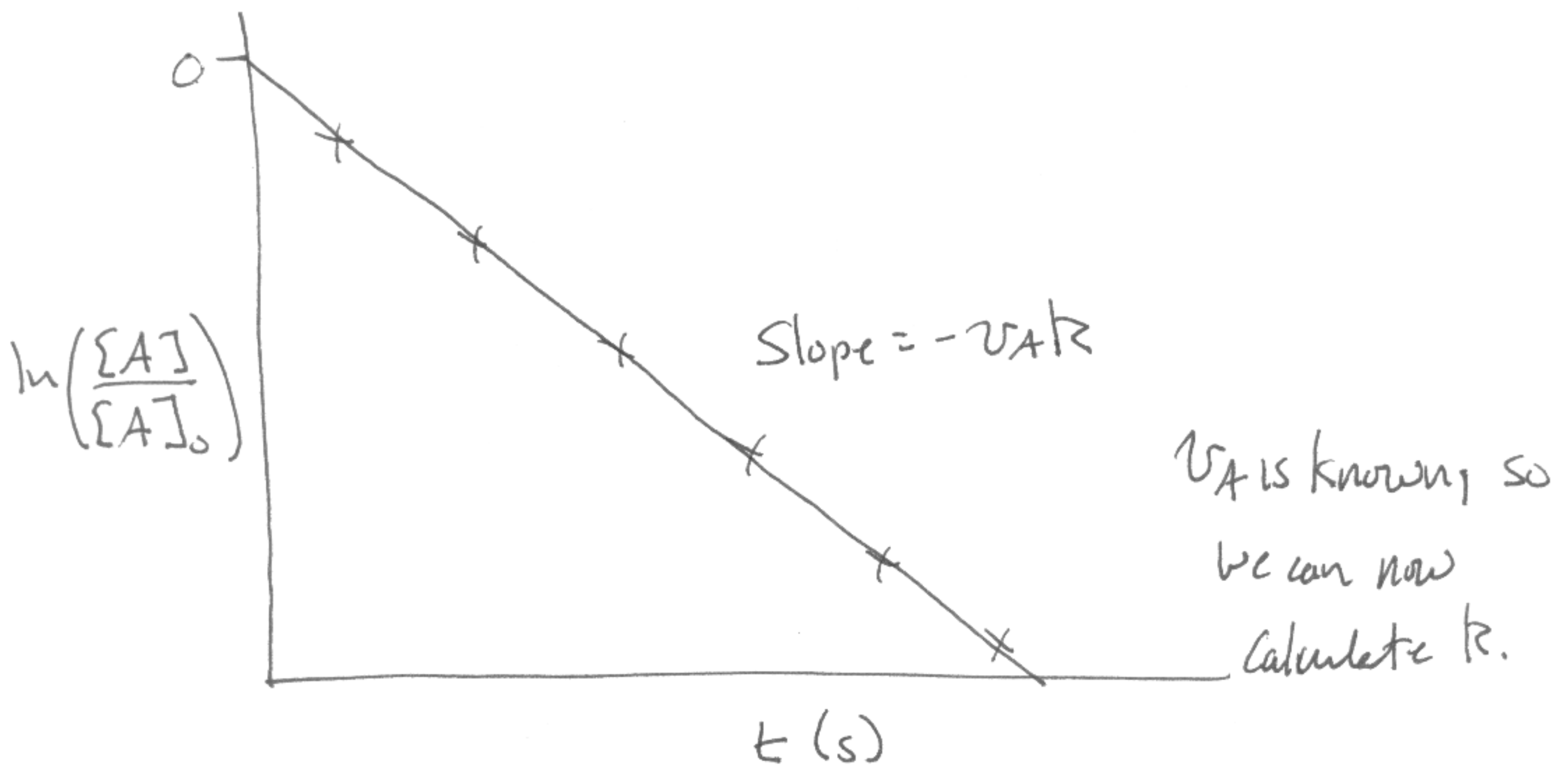
This is called an integrated rate law.

5. Our integrated rate law: $[A] = [A]_0 e^{-v_A k t}$

$$\text{or } \ln\left(\frac{[A]}{[A]_0}\right) = -v_A k t$$

If we plot $\ln\left(\frac{[A]}{[A]_0}\right)$ vs. t , we will plot a

Straight line of slope $-v_A k$.



*make sure you understand why the y-intercept of this figure is $\ln\left(\frac{[A]}{[A]_0}\right) = 0$ and why the slope is negative.