

## Exercise

E20B.2(b) The rate law is

$$v = -\frac{1}{2} \frac{d[A]}{dt} = k_r[A]$$

The half-life formula in eqn. 20B.2 is based on the assumption that

$$-\frac{d[A]}{dt} = k_r[A]$$

That is, it would be accurate to take the half-life from the table and say

$$t_{1/2} = \frac{\ln 2}{k_r'}$$

where  $k_r' = 2k_r$ . Thus

$$t_{1/2} = \frac{\ln 2}{2(3.56 \times 10^{-7} \text{ s}^{-1})} = \boxed{9.74 \times 10^5 \text{ s}}$$

Likewise, we modify the integrated rate law (eqn. 20B.1), noting that pressure is proportional to concentration:

$$p = p_0 e^{-2k_r t}$$

(i) Therefore, after 50 s, we have

$$p = (33.0 \text{ kPa}) e^{-2 \times (3.56 \times 10^{-7} \text{ s}^{-1}) \times (50 \text{ s})} = \boxed{32.999 \text{ kPa}}$$

(ii) After 20 min,

$$p = (33.0 \text{ kPa}) e^{-2 \times (3.56 \times 10^{-7} \text{ s}^{-1}) \times (20 \times 60 \text{ s})} = \boxed{32.97 \text{ kPa}}$$

E20B.4(b) The rate law is

$$v = -\frac{1}{2} \frac{d[A]}{dt} = k_r[A]^3$$

which integrates to

$$2k_r t = \frac{1}{2} \left( \frac{1}{[A]^2} - \frac{1}{[A]_0^2} \right) \quad \text{so} \quad t = \frac{1}{4k_r} \left( \frac{1}{[A]^2} - \frac{1}{[A]_0^2} \right)$$

$$t = \left( \frac{1}{4(6.50 \times 10^{-4} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1})} \right) \times \left( \frac{1}{(0.015 \text{ mol dm}^{-3})^2} - \frac{1}{(0.067 \text{ mol dm}^{-3})^2} \right) \\ = \boxed{1.6 \times 10^6 \text{ s}} = \boxed{19 \text{ days}}$$

**E20D.1(b)** The Arrhenius equation for two different temperatures can be rearranged to yield the activation energy:

$$E_a = \frac{R \ln \frac{k_{r,2}}{k_{r,1}}}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{4.01 \times 10^{-2}}{2.25 \times 10^{-3}}}{\left(\frac{1}{(273+29) \text{ K}} - \frac{1}{(273+37) \text{ K}}\right)}$$

$$= \boxed{5.62 \times 10^4 \text{ J mol}^{-1}} = \boxed{56.2 \text{ kJ mol}^{-1}}$$

With the activation energy in hand, the pre-exponential factor can be found from either rate constant by rearranging eqn. 20D.4.

$$A = k_r e^{E_a/RT} = (2.25 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) e^{5.62 \times 10^4 \text{ J mol}^{-1} / (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(273+29) \text{ K}}$$

$$A = \boxed{1.19 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

Computing  $A$  from both provides a useful check on the calculation.

$$A = k_r e^{E_a/RT} = (4.01 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) e^{5.62 \times 10^4 \text{ J mol}^{-1} / (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(273+37) \text{ K}}$$

$$A = \boxed{1.19 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

## Problem

**P20B.10** Since both reactions are first-order,

$$-\frac{d[A]}{dt} = k_1[A] + k_2[A] = (k_1 + k_2)[A]$$

so  $[A] = [A]_0 e^{-(k_1+k_2)t}$  [20B.1 with  $k_r = k_1 + k_2$ ]

We are interested in the yield of ketene,  $\text{CH}_2\text{CO}$ ; call it K:

$$\frac{d[K]}{dt} = k_2[A] = k_2[A]_0 e^{-(k_1+k_2)t}$$

Integrating yields

$$\int_0^{[K]} d[K] = k_2[A]_0 \int_0^t e^{-(k_1+k_2)t} dt$$

$$[K] = \frac{k_2[A]_0}{k_1 + k_2} (1 - e^{-(k_1+k_2)t}) = \frac{k_2}{k_1 + k_2} ([A]_0 - [A])$$

The percent yield is the amount of K produced compared to complete conversion; since the stoichiometry of reaction (2) is one-to-one, we can write:

$$\% \text{ yield} = \frac{[K]}{[A]_0} \times 100\% = \frac{k_2}{k_1 + k_2} (1 - e^{-(k_1+k_2)t}) \times 100\%$$

which has its maximum value when the reaction reaches completion

$$\max \% \text{ yield} = \frac{k_2}{k_1 + k_2} \times 100\% = \frac{4.65 \text{ s}^{-1}}{(3.74 + 4.65) \text{ s}^{-1}} \times 100\% = \boxed{55.4\%}$$

**P20B.12** The stoichiometry of the reaction relates product and reaction concentrations as follows:

$$[A] = [A]_0 - 2[B]$$

When the reaction goes to completion,  $[B] = [A]_0/2$ ; hence  $[A]_0 = 0.624 \text{ mol dm}^{-3}$ . We can therefore tabulate  $[A]$ , and examine its half-life. We see that the half-life of A from its initial concentration is approximately 20 min, and that its half-life from the concentration at 20 min is also 20 min. This indicates a first-order reaction. We confirm this conclusion by plotting the data accordingly (in Fig. 20B.4), using

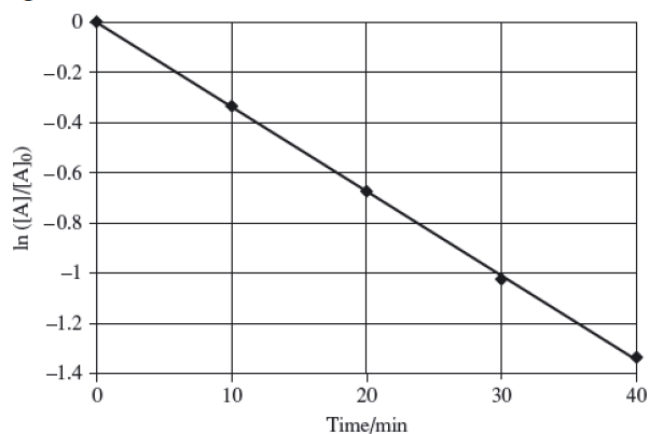
$$\ln \frac{[A]_0}{[A]} = k_A t \quad [20B.1]$$

which follows from

$$\frac{d[A]}{dt} = -k_A[A]$$

$t / \text{min}$	0	10	20	30	40	$\infty$
$[B]/(\text{mol dm}^{-3})$	0	0.089	0.153	0.200	0.230	0.312
$[A]/(\text{mol dm}^{-3})$	0.624	0.446	0.318	0.224	0.164	0
$\ln \frac{[A]}{[A]_0}$	0	-0.34	-0.67	-1.02	-1.34	

**Figure 20B.4**



The points lie on a straight line, which confirms first-order kinetics. Since the slope of the line is  $-3.4 \times 10^{-2} \text{ min}^{-1}$ , we conclude that  $k_A = 3.4 \times 10^{-2} \text{ min}^{-1}$ . To express the rate law in the form  $v = k_r[A]$  we note that

$$v = -\frac{1}{2} \frac{d[A]}{dt} = -\left(\frac{1}{2}\right) \times (-k_A[A]) = \frac{1}{2} k_A[A]$$

and hence  $k_r = \frac{1}{2} k_A = \boxed{1.7 \times 10^{-2} \text{ min}^{-1}}$

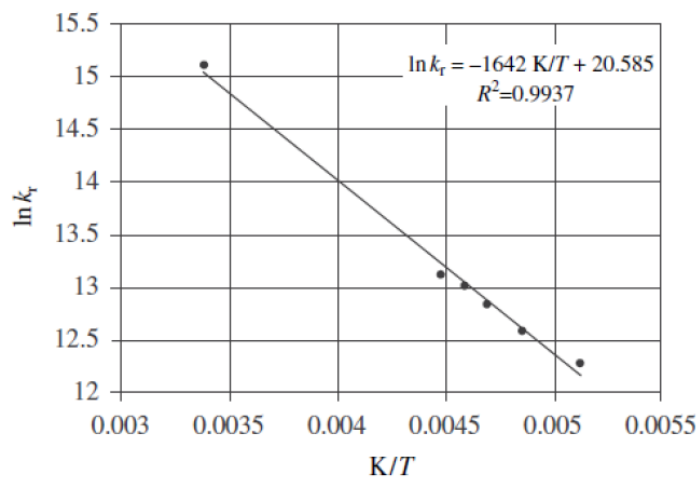
**P20D.4** The Arrhenius expression for the rate constant is (eqn. 20D.1)

$$\ln k_r = \ln A - E_a/RT$$

A plot of  $\ln k_r$  versus  $1/T$  will have slope  $-E_a/R$  and  $y$ -intercept  $\ln A$ . The transformed data and plot (Fig. 85.2) follow:

$T / \text{K}$	295	223	218	213	206	200	195
$10^{-6}k_r/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$	3.55	0.494	0.452	0.379	0.295	0.241	0.217
$\ln k_r/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$	15.08	13.11	13.02	12.85	12.59	12.39	12.29
$10^{-3} \text{K} / T$	3.39	4.48	4.59	4.69	4.85	5.00	5.13

Figure 20D.2



So  $E_a = -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-1642 \text{ K}) = 1.37 \times 10^4 \text{ J mol}^{-1} = \boxed{13.7 \text{ kJ mol}^{-1}}$   
 and  $A = e^{20.585} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = \boxed{8.7 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$

**P20E.4** Let the forward rates be written as

$$r_1 = k_1[A], \quad r_2 = k_2[B], \quad r_3 = k_3[C]$$

and the reverse rates as

$$r'_1 = k'_1[B], \quad r'_2 = k'_2[C], \quad r'_3 = k'_3[D]$$

The net rates are then

$$R_1 = k_1[A] - k'_1[B], \quad R_2 = k_2[B] - k'_2[C], \quad R_3 = k_3[C] - k'_3[D]$$

But  $[A] = [A]_0$  and  $[D] = 0$ , so that the steady-state equations for the net rates of the individual steps are

$$k_1[A]_0 - k'_1[B] = k_2[B] - k'_2[C] = k_3[C]$$

From the second of these equations we find

$$[C] = \frac{k_2[B]}{k'_2 + k_3}$$

After inserting this expression for  $[C]$  into the first of the steady-state equations we obtain

$$[B] = \frac{k_1[A]_0 + k_2'[C]}{k_1' + k_2} = \frac{k_1[A]_0 + k_2' \left( \frac{k_2[B]}{k_2' + k_3} \right)}{k_1' + k_2}$$

which yields, upon isolating [B],

$$[B] = [A]_0 \times \frac{k_1}{k_1' + k_2 - \left( \frac{k_2 k_2'}{k_2' + k_3} \right)}$$

Thus, at the steady-state

$$R_1 = R_2 = R_3 = [A]_0 k_1 \times \left( 1 - \frac{k_1}{k_1' + k_2 - \left( \frac{k_2 k_2'}{k_2' + k_3} \right)} \right) = \boxed{\frac{k_1 k_2 k_3 [A]_0}{k_1' k_2' + k_1' k_3 + k_2 k_3}}$$