INTRODUCTION TO NATURAL SCIENCE

CHEMISTRY HOMEWORK - WEEK 3 - SPRING 2007

Chapter 15

(7) 2nd order with respect to A
1st — " — B
total order = 2+1 = 3

(9) (a) rate = $k[NO_2][O_3]$

(b) rate = $k[NO_2][O_3]$

Initially let rate = r $[NO_2] = x$ $[O_3] = y$

$r = k(x)(y) = kxy$

When $[NO_2]$ is tripled $[NO_2] = 3x$

rate = $k(3x)y = k3xy = 3(kxy) = 3r$

= 3 × initial rate

(c) new rate = $k(x)\left(\frac{y}{2}\right) = \frac{1}{2}(kxy) = \frac{1}{2}r$

= $\frac{1}{2}$ (initial rate)

(11) (a) $rate = k[NO]^x [O_2]^y$

~~expt ①~~ $rate = -\frac{1}{2}\frac{\Delta[NO]}{\Delta t}$ ∴ rate

rate for expt ① $= \frac{1}{2}(2.5 \times 10^{-5})\, mol\, L^{-1} s^{-1}$

$= 1.25 \times 10^{-5}\, mol\, L^{-1} s^{-1}$

rate for expt ② $= \frac{1}{2}(1.0 \times 10^{-4})\, mol\, L^{-1} s^{-1}$

$= 0.5 \times 10^{-4}\, mol\, L^{-1} s^{-1}$

rate for expt ③ $= \frac{1}{2}(5.0 \times 10^{-5})\, mol\, L^{-1} s^{-1}$

$= 2.5 \times 10^{-5}\, mol\, L^{-1} s^{-1}$

<u>Expt ① data</u>

$rate = k[NO]^x [O_2]^y$

$1.25 \times 10^{-5} = k[0.010]^x [0.010]^y$ — ①

Expt ② data

$0.5 \times 10^{-4} = k[0.020]^x [0.010]^y$ — ②

Expt ③ data

$2.5 \times 10^{-5} = k[0.010]^x [0.020]^y$ — ③

$\frac{②}{①} \quad \frac{0.5 \times 10^{-4}}{1.25 \times 10^{-5}} = \frac{k[0.020]^x [0.010]^y}{k[0.010]^x [0.010]^y}$

$$4 = \left(\frac{0.020}{0.010}\right)^x = 2^x \Rightarrow \underline{\underline{x = 2}}$$

$$\frac{③}{①} \quad \frac{2.5\times10^{-5}}{1.25\times10^{-5}} = \frac{k\,(0.010)^x\,(0.020)^y}{k\,(0.010)^x\,(0.010)^y}$$

$$2 = 2^y \Rightarrow \underline{\underline{y = 1}}$$

Reaction is 2^{nd} order w.r.t. [NO] and 1^{st} order w.r.t. O_2.

(b) rate $= k[NO]^2[O_2]^1$

(c) expt ① rate $= k[NO]^2[O_2]^1$

$$k = \frac{1.25\times10^{-5}\ mol\ L^{-1}\ s^{-1}}{[0.010\ mol\ L^{-1}]^2\,[0.010](mol\ L^{-1})} = \underline{\underline{12.5\ mol^{-2}\ L^{2}\ s^{-1}}}$$

(d) rate $= k\,[NO]^2[O_2]$

$$= 12.5\ mol^{-2}\ L^2\ s^{-1}\,(0.015\ mol\ L^{-1})^2\,(0.0050\ mol/L)$$

$$= \underline{\underline{1.40\times10^{-5}\ mol\ L^{-1}\ s^{-1}}}$$

(e) NO is reacting twice as fast as O_2
NO$_2$ is appearing at the same rate as NO is disappearing.

∴ when rate of NO reacting $= 1.0\times10^{-4}\ mol\ L^{-1}s^{-1}$
rate at which O_2 reacts $= \frac{1}{2}(1.0\times10^{-4})\ mol\ L^{-1}s^{-1}$

$= \underline{\underline{5.0 \times 10^{-5}\ mol\ L^{-1} s^{-1}}}$

rate at which NO_2 appears $=$ $\underline{\underline{1.0 \times 10^{-4}\ mol\ L^{-1} s^{-1}}}$

(13) (a) rate $= k[NO]^x [O_2]^y$

expt ① $3.4 \times 10^{-8} = k[3.6 \times 10^{-4}]^x [5.2 \times 10^{-3}]^y$ — ①

expt ② $6.8 \times 10^{-8} = k[3.6 \times 10^{-4}]^x [1.04 \times 10^{-2}]^y$ — ②

expt ③ $1.7 \times 10^{-8} = k[1.8 \times 10^{-4}]^x [1.04 \times 10^{-2}]^y$ — ③

$\frac{②}{①} \Rightarrow 2 = 2^y \Rightarrow \underline{\underline{y = 1}}$

$$\frac{③}{①} \quad \frac{1.7 \times 10^{-8}}{3.4 \times 10^{-8}} = \left(\frac{1.8 \times 10^{-4}}{3.6 \times 10^{-4}}\right)^x \left(\frac{1.04 \times 10^{-2}}{5.2 \times 10^{-3}}\right)^y$$

$$0.5 = (0.5)^x (2)^y$$

$$\frac{0.5}{2} = (0.5)^x \qquad y = 1$$

$$0.25 = (0.5)^x$$

$$\ln 0.25 = x(\ln 0.5) = x(-0.693)$$

$$-1.39 = x(-0.693)$$

$$x = 2$$

$$\underline{\underline{\text{rate} = k[NO]^2 [O_2]}}$$

(b) substitute expt ① data into rate law

$$3.4 \times 10^{-8}\ mol\ L^{-1} h^{-1} = k\,(3.6\times10^{-4})^2 (5.2\times10^{-3})\ mol^3 L^{-3}$$

$$k = \frac{3.4\times10^{-8}\ mol\ L^{-1}\ h^{-1}}{(3.6\times10^{-4})^2 (5.2\times10^{-3})\ mol^3 L^{-3}} = \underline{\underline{50.45\ mol^{-2} L^2 h^{-1}}}$$

expt ④ rate = $k\,(1.8\times10^{-4})^2 (5.2\times10^{-3})\ mol^3 L^{-3}$

$$= 50.45\ mol^{-2} L^2 h^{-1}\ (1.8\times10^{-4})^2 (5.2\times10^{-3})\ mol^3 L^{-3}$$

$$= \underline{\underline{8.49\times10^{-9}\ mol\ L^{-1} h^{-1}}}$$

(18) first order r^n $\ln[A]_t - \ln[A]_0 = -kt$

$$\ln(2.50) - \ln(2.56) = -k\,(4.26\,min)$$

$$k = \frac{-2.37\times10^{-2}}{-4.26\,min} = \underline{\underline{5.57\times10^{-3}\ min^{-1}}}$$

(21) Rate = $k\,[NH_4NCO]^2 \Rightarrow$ r^n is 2^nd order

$$\therefore \frac{1}{[A]_t} = +kt + \frac{1}{[A]_0}$$

$$\frac{1}{0.180\ M} = (0.0113\ L\ mol^{-1} min^{-1})\,t + \frac{1}{0.229\ M}$$

$$\frac{1.1887\ M^{-1}}{0.0113\ L\ mol^{-1} min^{-1}} = t = \underline{\underline{105.2\ min}}$$

(26) for a first order $r^{=}$ $t_{1/2} = \frac{0.693}{k}$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{245 \text{ min}} = 2.829 \times 10^{-3} \text{ min}^{-1}$$

$$\ln [A]_t - \ln [A]_0 = -kt$$

$$\frac{\ln (2.00 \times 10^{-4}) - \ln (3.6 \times 10^{-3})}{-2.829 \times 10^{-3} \text{ min}^{-1}} = t$$

$$t = 1.022 \times 10^{3} \text{ min} = \underline{\underline{17.03 \text{ hrs}}}$$

(29) radioactive decay is a first order process.

$$t_{1/2} = \frac{0.693}{k} = 12.70 \text{ hrs}$$

$$k = \underline{\underline{5.457 \times 10^{-2} \text{ hr}^{-1}}}$$

$$\left(\frac{[A]_t}{[A]_0}\right) = e^{-kt}$$

$$\frac{[A]_t}{[A]_0} = e^{-(5.457 \times 10^{-2} \text{ hr}^{-1})(64 \text{ hr})} = \underline{\underline{3.04 \times 10^{-2}}}$$

Chapter 15	Problem # 33

(a)

time	[sucrose]	ln [sucrose]	1/[sucrose]
min	mol/L		L/mol
0	0.316	-1.152013065	3.164556962
39	0.274	-1.294627173	3.649635036
80	0.238	-1.435484605	4.201680672
140	0.190	-1.660731207	5.263157895
210	0.146	-1.924148657	6.849315068

Chapter 15	Problem # 38

time	[HOF]	ln [HOF]	1/[HOF]
min	mol/L		L/mol
0.00	0.850	-0.162518929	1.176470588
2.00	0.810	-0.210721031	1.234567901
5.00	0.754	-0.282362911	1.326259947
20.00	0.526	-0.642454066	1.901140684
50.00	0.243	-1.414693836	4.115226337

(b) Problem 33 Graph of ln [sucrose] vs time is a straight line

⇒ Reaction is 1st order. Rate = k [Sucrose]

Slope of graph = -3.67×10^{-3} min^{-1} = $-k$

$k = 3.67 \times 10^{-3}$ min^{-1}

(c) $\ln[\text{sucrose}]_t = -kt + \ln[\text{sucrose}]_0$

$= -(3.67 \times 10^{-3} \text{ min}^{-1})(175 \text{ min}) + \ln[0.316]$

$= -1.794$

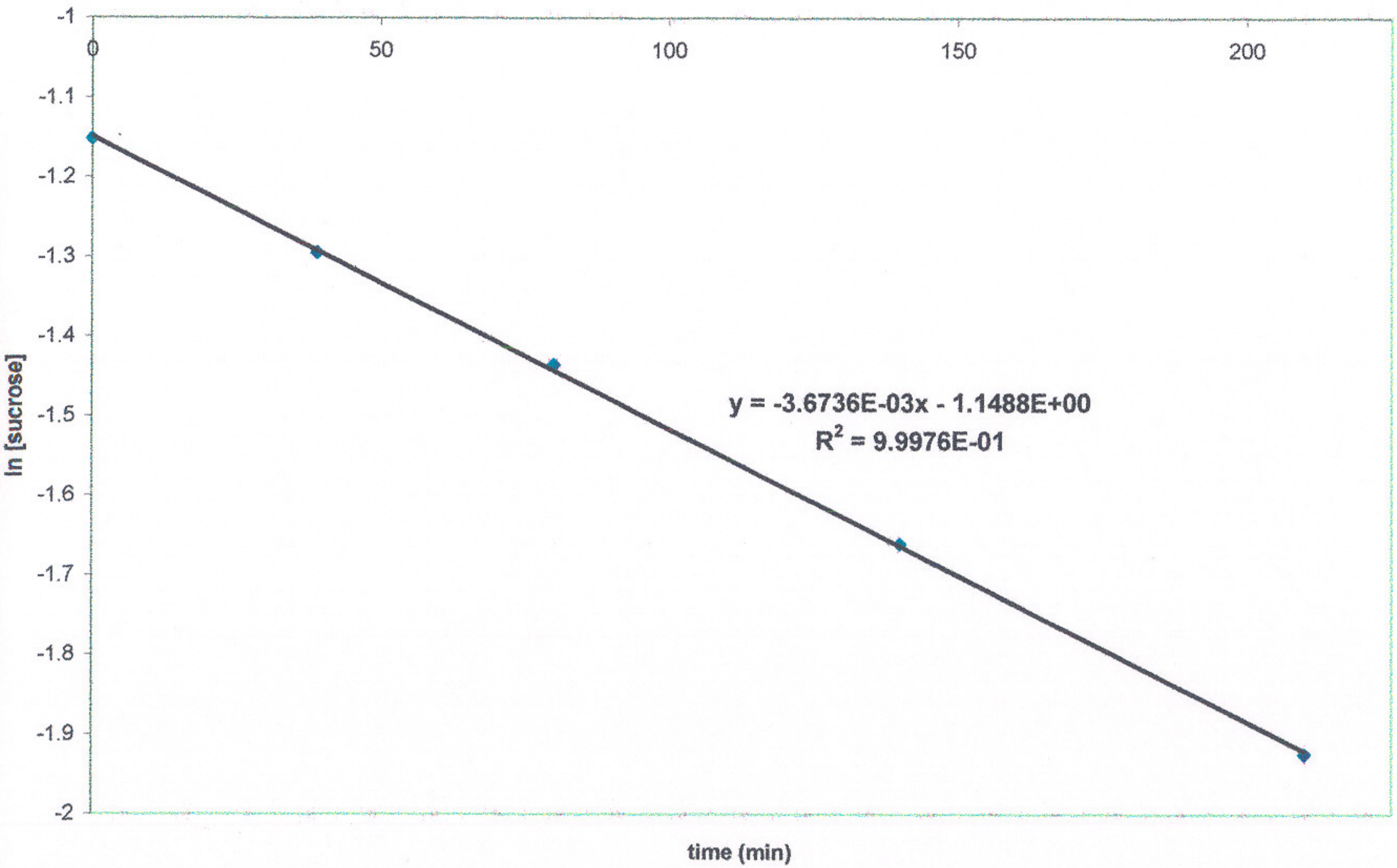
[sucrose] $= 0.166$ mol L^{-1}

Problem #38 Since the graph of ln [HOF] vs time is a straight line, the reaction is 1st order.

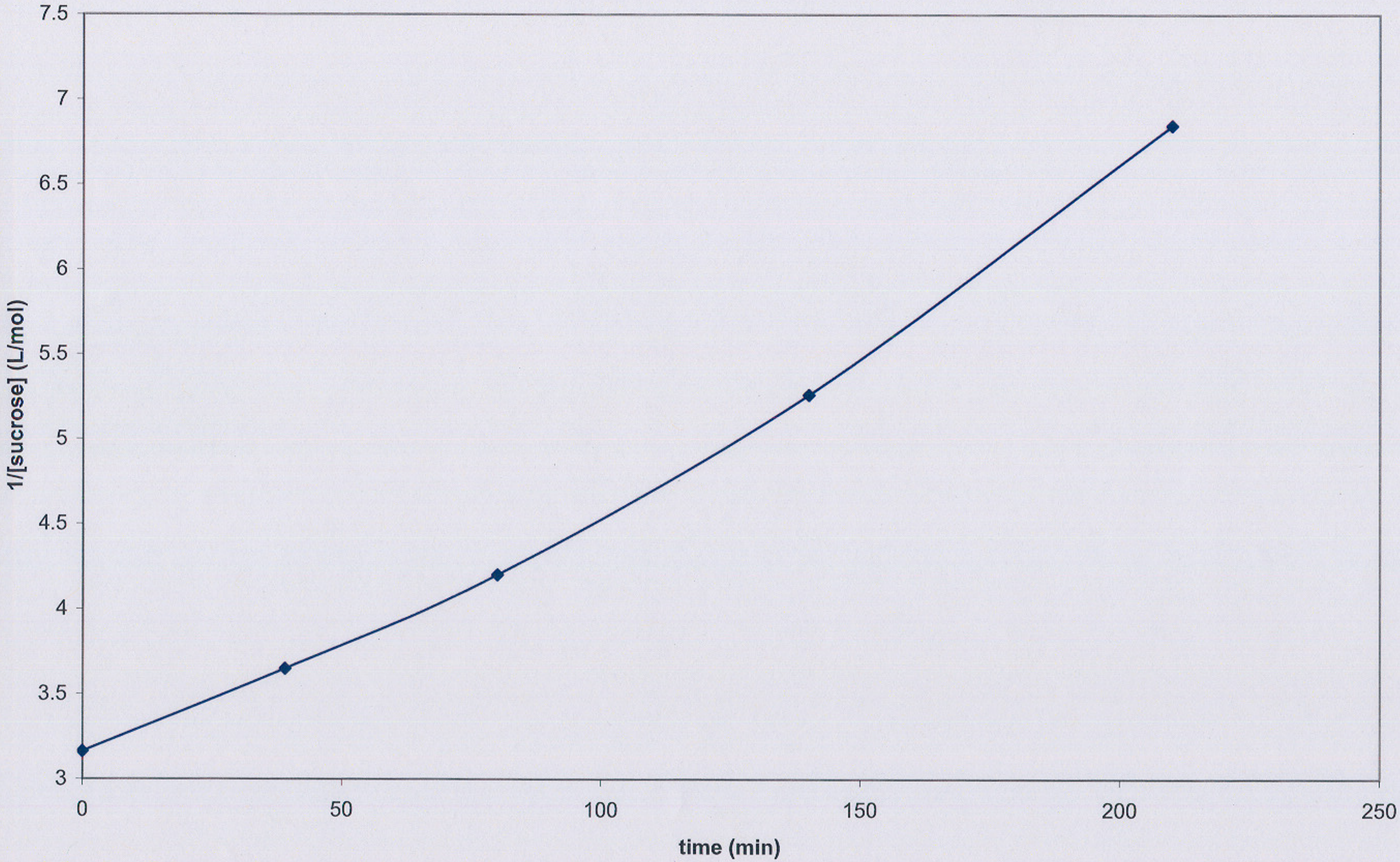
rate law: rate = k [HOF]

rate constant = −slope of graph = 0.025 min^{-1}

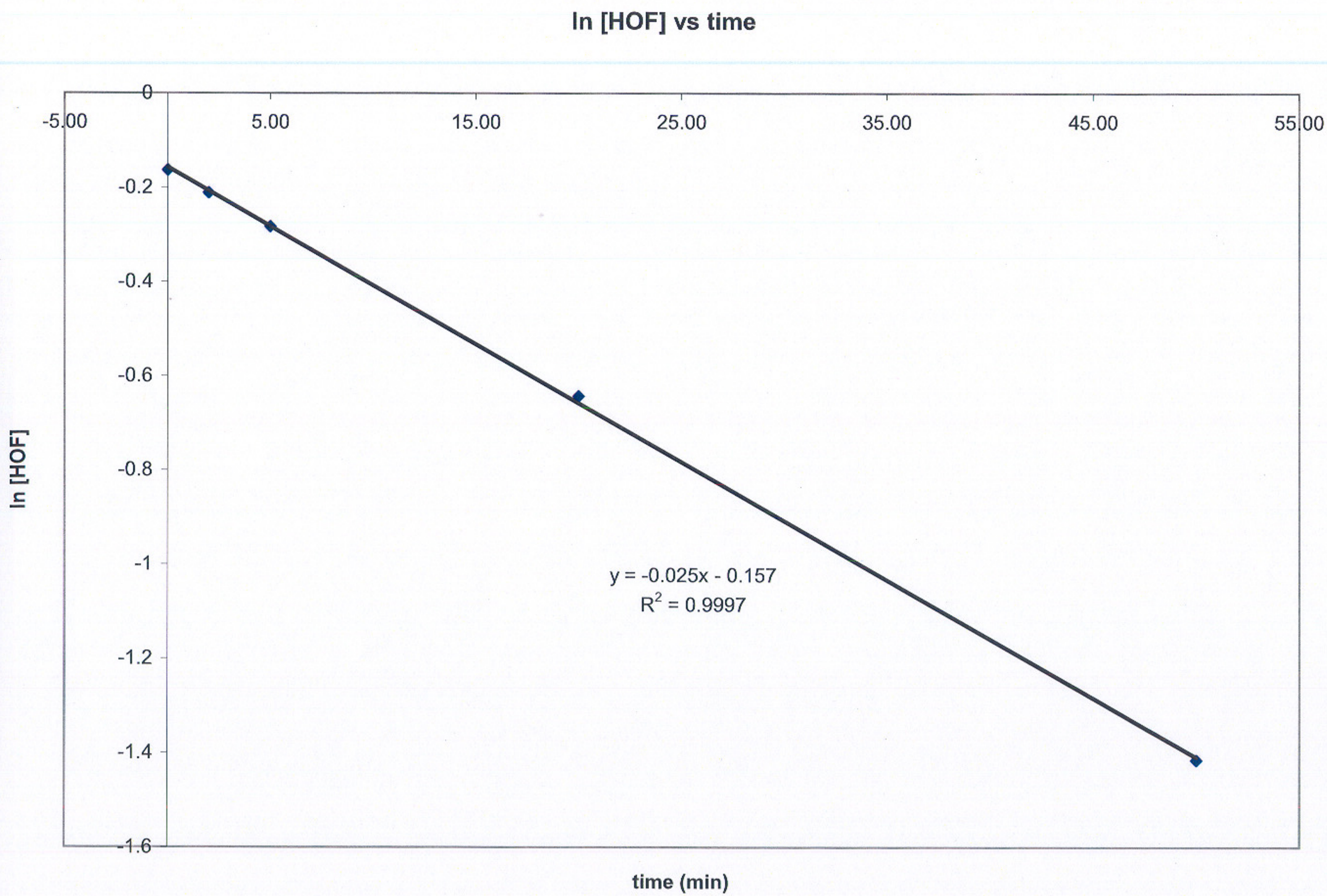
Problem # 33 graph of ln [sucrose] vs time



1/[sucrose] vs time , Problem #33

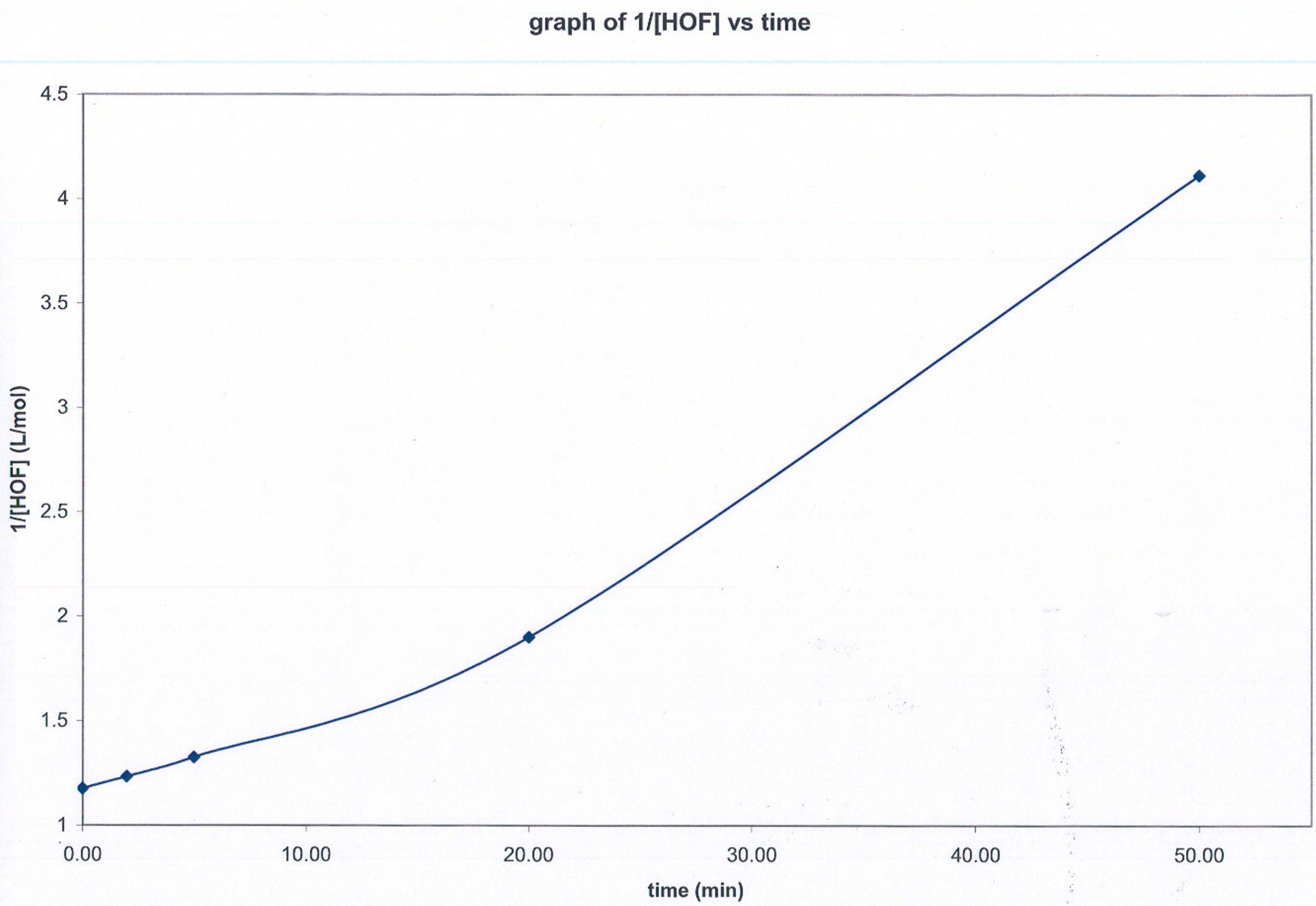


Problem #38



ln [HOF] vs time
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
-1.6
-5.00
5.00
15.00
25.00
35.00
45.00
55.00
ln [HOF]
y = -0.025x - 0.157
R2 = 0.9997
time (min)

Problem #38


graph of 1/[HOF] vs time
4.5
4
3.5
3
2.5
2
1.5
1
1/[HOF] (L/mol)
0.00
10.00
20.00
30.00
40.00
50.00
time (min)

(~~33~~) (41) $k = A e^{-Ea/RT}$

$3.46 \times 10^{-5}\, s^{-1} = A\, e^{-Ea/(8.314\, J K^{-1} mol^{-1})(298 K)}$

$3.46 \times 10^{-5}\, s^{-1} = A\, e^{-Ea/2.48 \times 10^{3}\, J mol^{-1}}$ —— (1)

$1.5 \times 10^{-3}\, s^{-1} = A\, e^{-Ea/(8.314\, J K^{-1} mol^{-1})(328 K)}$

$1.5 \times 10^{-3}\, s^{-1} = A\, e^{-Ea/2.73 \times 10^{3}\, J mol^{-1}}$ —— (2)

$\frac{(2)}{(1)}$ $\frac{1.5 \times 10^{-3}}{3.46 \times 10^{-5}} = e^{-Ea\left[\frac{J^{-1} mol}{2.73 \times 10^{3}} - \frac{J^{-1} mol}{2.48 \times 10^{3}}\right]}$

$43.353 = e^{+Ea[3.65 \times 10^{-5}\, J^{-1} mol^{-1}]}$

$\ln 43.353 = \ln E_a + \ln(3.65 \times 10^{-5})$

$3.769 = \ln E_a + (-1.022 \times 10^{1})$

$\ln E_a = 13.987$

$E_a = 1.187 \times 10^{6}\, J\, mol^{-1}$

(43) $k = A e^{-E_a/RT}$

$\ln k = \ln A - \frac{Ea}{RT}$

$\ln k_1 = \ln A - \frac{Ea}{RT_1}$ —— (1)

$\ln k_2 = \ln A - \frac{Ea}{RT_2}$ —— (2)

① − ② ⇒

$$\ln k_1 - \ln k_2 = \frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

let $T_1 = 800\ K$ $\quad k_1 = 0.0315\ s^{-1}$

$T_2 = 850\ K$ $\quad k_2 = ?$

$$\ln (0.0315) - \ln k_2 = \frac{260\ kJ\ mol^{-1}}{8.314\ J\ K^{-1}\ mol^{-1}}\left(\frac{10^3\ J}{kJ}\right)\left[\frac{1}{850K} - \frac{1}{800K}\right]$$

$$-3.458 \quad - \ln k_2 = -2.299$$

$$\ln k_2 = -1.159$$

$$k_2 = 3.14 \times 10^{-1}\ s^{-1}$$

(47) (a) rate = $k\ [NO][NO_3]$

(b) rate = $k\ [Cl][H_2]$

(c) rate = $k\ [(CH_3)_3CBr]$

(50) (a) $NO_2(g) + \cancel{NO_2(g)} \longrightarrow NO(g) + \cancel{NO_3(g)}$

$\cancel{NO_3(g)} + CO(g) \longrightarrow \cancel{NO_2(g)} + CO_2(g)$

$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

(b) step ① = 2

step ② = 2

(c) rate = $k[NO_2]^2$ rate is dependent on the slowest step; i.e. step ①.

(d) intermediates: NO_3 (g) (produced & consumed during the mechanism) a 8

Chapter 23

(12) (a) $^{54}_{26}Fe + ^{4}_{2}He \longrightarrow 2\,^{1}_{0}n + ^{56}_{28}Ni$

(b) $^{27}_{13}Al + ^{4}_{2}He \longrightarrow ^{30}_{15}P + ^{1}_{0}n$

(c) $^{32}_{16}S + ^{1}_{0}n \longrightarrow ^{1}_{1}H + ^{32}_{15}P$

(d) $^{96}_{42}Mo + ^{2}_{1}H \longrightarrow ^{1}_{0}n + ^{97}_{43}Tc$

(e) $^{98}_{42}Mo + ^{1}_{0}n \longrightarrow ^{99}_{43}Tc + ^{0}_{-1}\beta$

(f) $^{18}_{9}F \longrightarrow ^{18}_{8}O + ^{0}_{+1}\beta$

(15) (a) $^{19}_{10}Ne \longrightarrow ^{0}_{+1}\beta + ^{19}_{9}F$

(b) $^{59}_{26}Fe \longrightarrow ^{0}_{-1}\beta + ^{59}_{27}Co$

(c) $^{40}_{19}K \longrightarrow ^{0}_{-1}\beta + ^{40}_{20}Ca$

(d) $^{37}_{18}Ar + ^{0}_{-1}e$ (electron capture) $\longrightarrow ^{37}_{17}Cl$

(e) $^{55}_{26}Fe + ^{0}_{-1}e$ (electron capture) $\longrightarrow ^{55}_{25}Mn$

(f) $^{26}_{13}Al \longrightarrow ^{25}_{12}Mg + ^{1}_{1}p$

$^{1}_{1}p = ^{1}_{1}H$

b

(17)

$$^{232}_{90}Th \longrightarrow {}^{4}_{2}\alpha + {}^{228}_{88}Ra$$

$$^{228}_{88}Ra \longrightarrow {}^{0}_{-1}\beta + {}^{228}_{89}Ac$$

$$^{228}_{89}Ac \longrightarrow {}^{0}_{-1}\beta + {}^{228}_{90}Th$$

$$^{228}_{90}Th \longrightarrow {}^{4}_{2}\alpha + {}^{224}_{88}Ra$$

$$^{224}_{88}Ra \longrightarrow {}^{4}_{2}\alpha + {}^{220}_{86}Rn$$

$$^{220}_{86}Rn \longrightarrow {}^{4}_{2}\alpha + {}^{216}_{84}Po$$

$$^{216}_{84}Po \longrightarrow {}^{4}_{2}\alpha + {}^{212}_{82}Pb$$

$$^{212}_{82}Pb \longrightarrow {}^{0}_{-1}\beta + {}^{212}_{83}Bi$$

$$^{212}_{83}Bi \longrightarrow {}^{0}_{-1}\beta + {}^{212}_{84}Po$$

$$^{212}_{84}Po \longrightarrow {}^{4}_{2}\alpha + {}^{208}_{82}Pb$$