~~#~~ 7 HWK Key

Pg 1

28-2

$$2N_2O\,(g) \rightarrow 2N_2\,(g) + O_2\,(g)$$

$v(t) = 6.16 \times 10^{-6}$ mol/L·s @ 900K

$$v(t) = -\frac{1}{2}\frac{d[N_2O]}{dt} = \frac{1}{2}\frac{d[N_2]}{dt} = \frac{d[O_2]}{dt}$$

$$\frac{d[N_2O]}{dt} = -2(6.16 \times 10^{-6}) = -1.23 \times 10^{-5}\ \frac{mol}{L \cdot s}$$

$$\frac{d[N_2]}{dt} = 2(6.16 \times 10^{-6}) = 1.23 \times 10^{-5}\ mol/L \cdot s$$

$$\frac{d[O_2]}{dt} = 6.16 \times 10^{-6}\ mol/L \cdot s$$

28-8 $NO(g) + H_2(g) \rightarrow$ products

* use method of initial rates *

$P_0(H_2)$	$P_0(NO)$	v_0 torr/s
400	159	34
400	300	125
289	400	160
205	400	110
147	400	79

$$v = k[NO]^{m_{NO}}[H_2]^{m_{H_2}}$$

$$\frac{125 = \cancel{k}[300]^{m_{NO}}\cancel{[400]^{m_{H_2}}}}{34 = \cancel{k}[159]^{m_{NO}}\cancel{[400]^{m_{H_2}}}} \qquad m_{NO} = \frac{\ln(34/125)}{\ln(159/300)} \approx 2$$

$$\frac{79 = \cancel{k[400]^2}[147]^{m_{H_2}}}{110 = \cancel{k[400]^2}[205]^{m_{H_2}}} \qquad m_{H_2} = \frac{\ln(110/79)}{\ln(205/147)} \approx 1$$

$$V = K[NO]^2[H_2]$$

Now find k... $k = \dfrac{v}{[NO]^2[H_2]}$

v_0	34	125	160	110	79
k	3.36×10^{-6}	3.47×10^{-6}	3.46×10^{-6}	3.35×10^{-6}	3.36×10^{-6}

$$k_{Ave} = 3.40\times10^{-6}\ \text{torr}^{-2}\cdot s^{-1}$$

28-10

$$Cr(H_2O)_6^{3+} + SCN^- \rightarrow Cr(H_2O)_5(SCN)^{2+} + H_2O$$

$$V = K[Cr(H_2O)_6^{3+}]^{m_{cr}}[SCN^-]^{m_{SCN}}$$

$$\frac{2.11\times10^{-11} = \cancel{K}[1.21\times10^{-4}]^{m_{cr}}\cancel{[1.05\times10^{-5}]^{m_{SCN}}}}{2.82\times10^{-11} = \cancel{K}[1.66\times10^{-4}]^{m_{cr}}\cancel{[1.02\times10^{-5}]^{m_{SCN}}}}$$

$$m_{cr} = \frac{\ln(2.11\times10^{-11}/2.82\times10^{-11})}{\ln(1.21\times10^{-4}/1.66\times10^{-4})} \approx 1$$

$$\frac{2.11\times10^{-11} = \cancel{K}[1.21\times10^{-4}]^{m_{cr}}[1.05\times10^{-5}]^{m_{SCN}}}{5.53\times10^{-11} = K[1.46\times10^{-4}][2.28\times10^{-5}]^{m_{SCN}}}$$

$$0.382 = 0.8288\,(0.4605)^{m_{SCN}}$$

$$0.461 = (0.461)^{m_{SCN}}$$

$$m_{SCN} = 1$$

$$V = K[Cr(H_2O)_6^{3+}][SCN^-]$$

V_0	2.11×10^{-11}	5.53×10^{-11}	2.82×10^{-11}	9.44×10^{-11}
K	0.0166	0.0164	0.0167	0.0166

$$\boxed{k_{Av} = 0.0166\ \frac{dm^3}{mol\cdot s}}$$

28-15 1^{st} order rxn $\ln \frac{[A]}{[A]_0} = -kt$

If $[A_0] = 1$ then $[A] = 0.\cancel{24}76$

$\ln(0.76/1) = -k(19.7)$

$k = 1.39 \times 10^{-2}\ \text{min}^{-1}$

If $[A]_0 = 1$ then $[A] = 0.145$

$\ln\left(\frac{0.145}{1}\right) = -1.39 \times 10^{-2}\ t$

$t = 139$ min

28-26 $UO_2(NO_3)_2 \rightarrow UO_3 + 2NO_2 + \frac{1}{2}O_2$

Plot $\ln[UO_2(NO_3)_2]$ vs t ... see attached Excel

b/c 1st order

$k =$ min^{-1}

28-28 $2N_2O \rightarrow 2N_2 + O_2$ ... Second order in $[N_2O]$

Plot $1/[N_2O]$ vs t ... See attached Excel

$k =$ mol/L·s

28-39 Yes, $k = A\underbrace{e^{-E_a/RT}}_{\text{unitless}}$ so k + A must have same units

28-48 $k = A e^{-E_a/RT}$

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

$$\ln(6.015\times10^{-5}) = \ln A - \frac{E_a}{R\cdot420} \qquad \ln(2.971\times10^{-3}) = \ln A - \frac{E_a}{R\cdot470}$$

$$\ln A = 2.971\times10^{-3} + \frac{E_a}{R\cdot470}$$

$$\overset{-9.72}{\cancel{6.015\times10^{-5}}} = \overset{-5.87}{\cancel{2.971\times10^{-3}}} - \frac{E_a}{R\cdot420} + \frac{E_a}{R\cdot470}$$

$$-\overset{3.8998}{\cancel{2.91\times10^{-3}}} = E_a\left(\frac{1}{R\cdot470} - \frac{1}{R\cdot420}\right)$$

$$E_a = \overset{-3.899}{\cancel{2.91\times10^{-3}}} / -3.05\times10^{-5}$$

$$\boxed{E_a = \cancel{95.6}\ 127.9 \text{ kJ/mol}}$$

$$\boxed{\text{So } A = 4.80\times10^{11}\ 1/\text{s}}$$

Eqn 28.76...

$$\frac{d\ln k}{dT} = \frac{1}{T} + \frac{\Delta^\ddagger U^\circ}{RT^2} = \frac{E_a}{RT^2} \quad \leftarrow \text{Eq 28.55}$$

$$\Delta^\ddagger H^\circ = \Delta^\ddagger U^\circ + RT\Delta^\ddagger n \to 0$$

together... $\frac{E_a}{RT^2} = \frac{1}{T} + \frac{\Delta^\ddagger H^\circ}{RT^2}$ or $E_a = RT + \Delta^\ddagger H^\circ$

w/ data @ 420 K... $\Delta^\ddagger H^\circ = 124.4$ kJ/mol
@ 470 K... $\Delta^\ddagger H^\circ = 124.0$ kJ/mol

Use Eq 28.74 to find $\Delta^\ddagger S^\circ$...

$$6.015\times10^{-5} = \frac{1.38\times10^{-23}\cdot420}{6.626\times10^{-34}\cdot1}\, e^{-124400/8.314\cdot420}\, e^{\Delta S^{\ddagger\circ}/R}$$

$$\ln(0.0203) = \Delta^\ddagger S^\circ/R$$

$$\Delta^\ddagger S^\circ = -32.4 \text{ J/mol}\cdot\text{K}$$

29-4 overall: $NO_2 + CO \rightarrow CO_2 + NO$

$$\frac{d[CO_2]}{dt} = k_{obs}[NO_2]^2$$

Proposed mechanism

① $NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO$ rate determining step

② $NO_3 + CO \xrightarrow{k_2} CO_2 + NO_2$

Since ① is rate determining step,

$$\frac{d[CO_2]}{dt} = k_1[NO_2]^2 \qquad k_{obs} = k_1$$

29-11

$$2N_2O_5 \xrightarrow{k_{obs}} 4NO_2 + O_2$$

proposed mechanism $N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} NO_2 + NO_3$

$$NO_2 + NO_3 \xrightarrow{k_2} NO + NO_2 + O_2$$

$$NO_3 + NO \xrightarrow{k_3} 2NO_2$$

$$\frac{d[NO]}{dt} = k_2[NO_2]\overset{[NO_3]}{} - k_3[NO][NO_3] = 0 \qquad \text{S.S.A.}$$

$$k_2[NO_2] = k_3[NO]$$

$$[NO] = \frac{k_2[NO_2]}{k_3}$$

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_2[NO_2][NO_3] - k_{-1}[NO_2][NO_3] - k_3[NO_3][NO] = 0$$

$$k_1[N_2O_5] = [NO_3](k_{-1}[NO_2] + k_2[NO_2] + k_3[NO])$$

$$[NO_3] = \frac{k_1[N_2O_5]}{k_{-1}[NO_2] + k_2[NO_2] + k_3[NO]} = \frac{k_1[N_2O_5]}{k_{-1}[NO_2] + k_2[NO_2] + k_2[NO_2]}$$

$\frac{k_2}{k_3}[NO_2]$

$$[NO_3] = \frac{k_1}{2k_2 + k_{-1}} \frac{[N_2O_5]}{[NO_2]}$$

$$\frac{d[O_2]}{dt} = k_2 [NO_2][NO_3]$$

$$= k_2 [\cancel{NO_2}] \frac{k_1}{2k_2+k_{-1}} \frac{[N_2O_5]}{[\cancel{NO_2}]}$$

if $k_{obs} = \frac{k_1 k_2}{2k_2 + k_{-1}}$

$$\frac{d[O_2]}{dt} = k_{obs} [N_2O_5]$$

28-13 $O_2NNH_2 \xrightarrow{k_{obs}} N_2O + H_2O$

$$\frac{d[N_2O]}{dt} = k_{obs} \frac{[O_2NNH_2]}{[H^+]}$$

mechanism

$O_2NNH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2NNH^- + H^+$ fast eq

$O_2NNH^- \xrightarrow{k_2} N_2O + OH^-$ slow

$H^+ + OH^- \xrightarrow{k_3} H_2O$ fast

$$K_c = \frac{k_1}{k_{-1}} = \frac{[O_2NNH^-][H^+]}{[O_2NNH_2]} \qquad [O_2NNH^-] = \frac{k_1}{k_{-1}} \frac{[O_2NNH_2]}{[H^+]}$$

$$\frac{d[N_2O]}{dt} = k_2 [O_2NNH^-]$$

$$= \frac{k_2 k_1}{k_{-1}} \frac{[O_2NNH_2]}{[H^+]}$$

$$\frac{d[N_2O]}{dt} = k_{obs} \frac{[O_2NNH_2]}{[H^+]} \qquad k_{obs} = k_2 K_c = \frac{k_2 k_1}{k_{-1}}$$

~~28~~ 29-14

$$\frac{d[O_2NNH^-]}{dt} = k_1[O_2NNH_2] - k_{-1}[O_2NNH^-][H^+] - k_2[O_2NNH^-] = 0$$

$$[O_2NNH^-](k_{-1}[H^+] + k_2) = k_1[O_2NNH_2]$$

$$\frac{d[N_2O]}{dt} = k_2[O_2NNH^-]$$

$$= k_2 \frac{k_1[O_2NNH_2]}{k_{-1}[H^+] + k_2}$$

If $k_2 << k_{-1}[H^+]$, this rate matches that of 28-13.

~~28~~ 29-24

Initiation: $CH_3CHO \xrightarrow{k_1} CH_3 + CHO$

Propagation: $CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO$

$CH_3CO \xrightarrow{k_3} CH_3 + CO$

Termination: $2CH_3 \xrightarrow{k_4} C_2H_6$

$$\frac{d[CH_4]}{dt} = k_2[CH_3][CH_3CHO]$$

$$\frac{d[CH_3]}{dt} = k_1[CH_3CHO] - k_2[CH_3][CH_3CHO] + k_3[CH_3CO] - k_4[CH_3]^2$$

$$\frac{d[CH_3CO]}{dt} = k_2[CH_3][CH_3CHO] - k_3[CH_3CO]$$

Steady state for CH_3 + CH_3CO...

$$\frac{d[CH_3]}{dt} = 0 = k_1[CH_3CHO] - k_2[CH_3][CH_3CHO] + k_3[CH_3CO] - k_4[CH_3]^2$$

$$\frac{d[CH_3CO]}{dt} = 0 = k_2[CH_3][CH_3CHO] - k_3[CH_3CO]$$

$$[CH_3CO] = \frac{k_2}{k_3}[CH_3][CH_3CHO]$$

$$0 = k_1 [CH_3CHO] - k_2 \cancel{[CH_3]}[CH_3CHO] + k_2 [CH_3]\cancel{[CH_3CHO]} - k_4 [CH_3]^2$$

$$[CH_3] = \left(\frac{k_1}{k_4}\right)^{1/2} [CH_3CHO]^{1/2}$$

plug in. –

$$\frac{d[CH_4]}{dt} = k_2 \left(\frac{k_1}{k_4}\right)^{1/2} [CH_3CHO]^{1/2} [CH_3CHO]$$

$$= k_2 \left(\frac{k_1}{k_4}\right)^{1/2} [CH_3CHO]^{3/2}$$

For presentation (12/12/07)

28-10

29-13

29-14