1. 第一次作业

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1.1. 2.1.

$$r \propto [\mathrm{A}] \wedge r \propto [\mathrm{B}]^{1/2} \implies \tag{1.1}$$

$$r = k[\mathrm{A}][\mathrm{B}]^{1/2}, \tag{1.2}$$

$$\text{order} = \frac{3}{2}. \tag{1.3}$$

1.2. 2.9.

For a consecutive reaction $[\mathrm{A}] \xrightarrow{k_1} [\mathrm{B}] \xrightarrow{k_2} [\mathrm{C}]$:

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_1[\mathrm{A}] \implies \tag{1.4}$$

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} -\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]} = \int_0^t k_1\,\mathrm{d}t \implies \tag{1.5}$$

$$\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} = k_1 t \implies \tag{1.6}$$

$$\boxed{[\mathrm{A}]_t = [\mathrm{A}]_0 \exp[-k_1 t]}, \tag{1.7}$$

$$-\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_2[\mathrm{B}] - k_1[\mathrm{A}] \implies \tag{1.8}$$

$$-\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_2[\mathrm{B}] - k_1[\mathrm{A}]_0\exp[-k_1 t], \tag{1.9}$$

we know that the solution of homogeneous equation is $[\mathrm{B}] = \exp[-k_2 t]$, now let $[\mathrm{B}] = f[t]\exp[-k_2 t]$:

$$-\frac{\mathrm{d}(f[t]\exp[-k_2 t])}{\mathrm{d}t} = k_2 f[t]\exp[-k_2 t] - k_1[\mathrm{A}]_0\exp[-k_1 t] \implies \tag{1.10}$$

$$-f[t](-k_2\exp[-k_2 t]) - f'[t]\exp[-k_2 t] = k_2 f[t]\exp[-k_2 t] - k_1[\mathrm{A}]_0\exp[-k_1 t] \implies \tag{1.11}$$

$$f'[t]\exp[-k_2 t] = k_1[\mathrm{A}]_0\exp[-k_1 t] \implies \tag{1.12}$$

$$\int_0^{f[t]} \mathrm{d}f = \int_0^t k_1[\mathrm{A}]_0\exp[(k_2-k_1)t]\,\mathrm{d}t \implies \tag{1.13}$$

$$f[t] = \frac{k_1[\mathrm{A}]_0}{k_2-k_1}\exp[(k_2-k_1)t]\Big|_0^t = \frac{k_1[\mathrm{A}]_0}{k_2-k_1}(\exp[(k_2-k_1)t]-1) \implies \tag{1.14}$$

$$\boxed{[\mathrm{B}]_t = \frac{k_1[\mathrm{A}]_0}{k_2-k_1}(\exp[-k_1 t]-\exp[-k_2 t])}. \tag{1.15}$$

Now if $[\mathrm{B}]_t$ is small relative to $[\mathrm{A}]_0$, which means the perturbation by vibration of [A] :

$$\frac{\partial[\mathrm{B}]_t}{\partial[\mathrm{A}]_0} = \frac{k_1}{k_2 - k_1}(\exp[-k_1 t] - \exp[-k_2 t]) \tag{1.16}$$

is minute. A reansonable mechanism is that $k_1 \ll k_2$.

1.3. 2.25.

We could detect that the compound $\mathrm{NO_3}$ is very reactive, which means the steady-state approximation could be applied:

$$\begin{cases} -\dfrac{\mathrm{d}[\mathrm{N_2O_5}]}{\mathrm{d}t} = k_1[\mathrm{N_2O_5}] - k_{-1}[\mathrm{NO_2}][\mathrm{NO_3}], \\ -\dfrac{\mathrm{d}[\mathrm{NO_3}]}{\mathrm{d}t} = k_{-1}[\mathrm{NO_2}][\mathrm{NO_3}] - k_1[\mathrm{N_2O_5}] + k_2[\mathrm{NO_2}][\mathrm{NO_3}] + k_3[\mathrm{NO}][\mathrm{NO_3}] = 0, \end{cases} \tag{1.17}$$

we now assume that NO is also reactive:

$$-\frac{\mathrm{d}[\mathrm{NO}]}{\mathrm{d}t} = k_3[\mathrm{NO}][\mathrm{NO_3}] - k_2[\mathrm{NO_2}][\mathrm{NO_3}] = 0 \implies \tag{1.18}$$

$$k_1[\mathrm{N_2O_5}] = k_{-1}[\mathrm{NO_2}][\mathrm{NO_3}] + 2k_2[\mathrm{NO_2}][\mathrm{NO_3}] \implies \tag{1.19}$$

$$[\mathrm{NO_2}][\mathrm{NO_3}] = \frac{k_1}{k_{-1} + 2k_2}[\mathrm{N_2O_5}] \implies \tag{1.20}$$

$$-\frac{\mathrm{d}[\mathrm{N_2O_5}]}{\mathrm{d}t} = (k_1 - \frac{k_{-1}k_1}{k_{-1} + 2k_2})[\mathrm{N_2O_5}] \equiv k[\mathrm{N_2O_5}], \tag{1.21}$$

$$k = k_1 - \frac{k_{-1}k_1}{k_{-1} + 2k_2}. \tag{1.22}$$

1.4. 2.30.

a.

$$\begin{cases} -\dfrac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_1[\mathrm{A}], \\ -\dfrac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_2[\mathrm{B}][\mathrm{A}] - k_1[\mathrm{A}], \\ -\dfrac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} - -k_2[\mathrm{B}][\mathrm{A}]. \end{cases} \tag{1.23}$$

b.

$$[\mathrm{A}] = [\mathrm{A}]_0 \exp[-k_1 t], \tag{1.24}$$

$$[\mathrm{B}] = \frac{k_1}{k_2}, \tag{1.25}$$

$$[\mathrm{C}] = [\mathrm{A}]_0 - [\mathrm{A}]_0 \exp[-t] - \frac{k_1}{k_2}. \tag{1.26}$$

The steady-state approximation condition makes [B] a constant, which inevitably conflicts with the condition where the initial concentration is 0.

c.

$$k_2[\mathrm{A}]_0 \gg k_1. \tag{1.27}$$

d.

$$[\mathrm{A}]_t = [\mathrm{A}]_0 \exp[-k_1 t], \tag{1.28}$$

$$[\mathrm{B}]_t = \frac{k_1}{k_2} + f[t] \implies \tag{1.29}$$

$$-\frac{\mathrm{d}f}{\mathrm{d}t} = k_2 f[\mathrm{A}] = k_2[\mathrm{A}]_0 \exp[-k_1 t] \implies \tag{1.30}$$

$$\int_{-k_1/k_2}^{f[t]} -\mathrm{d}\ln f = \int_0^t k_2[\mathrm{A}]_0 \exp[-k_1 t]\,\mathrm{d}t \implies \tag{1.31}$$

$$\ln\frac{-k_1/k_2}{f[t]} = \frac{k_2[\mathrm{A}]_0 \exp[-k_1 t]}{k_1} - \frac{k_2[\mathrm{A}]_0}{k_1} \implies \tag{1.32}$$

$$[\mathrm{B}]_t = -\frac{k_1}{k_2}\exp[\frac{k_2[\mathrm{A}]_0 \exp[-k_1 t]}{k_1} - \frac{k_2[\mathrm{A}]_0}{k_1}] + \frac{k_1}{k_2}, \tag{1.33}$$

$$[\mathrm{C}]_t = [\mathrm{A}]_0 - [\mathrm{A}]_t - [\mathrm{B}]_t. \tag{1.34}$$

e.

$$\lim_{t\to\infty}[\mathrm{B}]_t = -\frac{k_1}{k_2}\exp[-\frac{k_2[\mathrm{A}]_0}{k_1}] + \frac{k_1}{k_2}, \tag{1.35}$$

$$k_1[\mathrm{A}]_0 \gg k_1 \implies \tag{1.36}$$

$$\lim_{t\to\infty}[\mathrm{B}]_t = \frac{k_1}{k_2}(1 - \exp[-\infty]) = \frac{k_1}{k_2}. \tag{1.37}$$

2. 第二次作业

2.1. 1.1

On the basis of collision theory:

$$p = \frac{Nm\bar{v}^2}{3V}, \tag{2.1}$$

after the replacement:

$$p' = \frac{Nm\bar{v}^2}{6V} + \frac{N\frac{m}{2}(2\bar{v})^2}{6V} > p, \tag{2.2}$$

i.e. increase.

2.2. 1.8.

Maxwell-Boltzmann speed distribution:

$$f[v]\,\mathrm{d}v = \frac{4}{\sqrt{\pi}}\left(\frac{m\beta}{2}\right)^{3/2} v^2\,\mathrm{d}v\mathrm{e}^{-\beta\epsilon}, \tag{2.3}$$

$$\frac{\mathrm{d}f[v]}{\mathrm{d}v} = \frac{4}{\sqrt{\pi}}\left(\frac{m\beta}{2}\right)^{3/2} \partial_v(v^2\exp[-\frac{\beta mv^2}{2}]) = 0 \implies \tag{2.4}$$

$$v^2(-\beta mv\exp[-\frac{\beta mv^2}{2}]) + 2v\exp[-\frac{\beta mv^2}{2}] = 0 \implies \tag{2.5}$$

$$v^2\beta m = 2 \implies \tag{2.6}$$

$$v = \sqrt{\frac{2}{m\beta}}. \tag{2.7}$$

2.3. 1.16.

Maxwell-Boltzmann speed distribution:

$$f[v]\,\mathrm{d}v = \frac{4}{\sqrt{\pi}}\left(\frac{m\beta}{2}\right)^{3/2} v^2\,\mathrm{d}v\mathrm{e}^{-\beta\epsilon}, \tag{2.8}$$

$$\langle v^4\rangle = \int v^4 f[v]\,\mathrm{d}v = \frac{4}{\sqrt{\pi}}\left(\frac{m\beta}{2}\right)^{3/2}\int_0^\infty v^6\exp[-\beta\frac{1}{2}mv^2]\,\mathrm{d}v = 15(m\beta)^{-2}, \tag{2.9}$$

$$\beta = \frac{1}{k_\mathrm{B}T}, m = \frac{M}{N_\mathrm{A}}. \tag{2.10}$$

NOTES

$$\int_0^\infty x^{2n}\exp[-\alpha x^2]\,\mathrm{d}x = \frac{\sqrt{\pi}}{2}\frac{(2n)!\alpha^{-(n+\frac{1}{2})}}{2^{2n}n!}, \tag{2.11}$$

$$\int_0^\infty x^{2n+1}\exp[-\alpha x^2]\,\mathrm{d}x = \frac{1}{2}n!\alpha^{-(n+1)}, \tag{2.12}$$

3. 第三次作业

3.1. 3.1.

$$3N = 15. \tag{3.1}$$

3.2. 3.3

$$k = \langle k[\epsilon_\mathrm{r}] \rangle = \int \sigma v_\mathrm{r} f[\epsilon_\mathrm{r}]\,\mathrm{d}\epsilon_\mathrm{r} \implies \tag{3.2}$$

$$(\mathrm{d}). \tag{3.3}$$

3.3. 3.11.

a.

$$A \approx \pi b_{\mathrm{max}}^2 N_\mathrm{A} \sqrt{\frac{8RT}{\pi M_\mu}}, \tag{3.4}$$

$$b_{\mathrm{max}} = 0.34\mathrm{e} - 9, \tag{3.5}$$

$$M_\mu = \frac{30.01 \times 48}{30.01 + 48}\mathrm{e} - 3, \tag{3.6}$$

$$A = 128267273.9. \tag{3.7}$$

b.

$$A_{\mathrm{fact}} = pA \implies \tag{3.8}$$

$$p = 7.796\mathrm{e} - 4. \tag{3.9}$$

3.4. 3.13.

a.

$$\sigma = \pi d^2 \implies \tag{3.10}$$

$$r_{\mathrm{H}_2} = 1.4658\mathrm{e} - 10, r_\mathrm{F} = 1.1968\mathrm{e} - 10, \tag{3.11}$$

$$b_{\mathrm{max}} = 2.6626\mathrm{e} - 10, \tag{3.12}$$

$$A = 24955977.5, \tag{3.13}$$

$$A_{\mathrm{fact}} = 2\mathrm{e} + 8, p = 0.8015. \tag{3.14}$$

b.

$$k = \frac{k_{\mathrm{B}}T}{h}\frac{q^{\ddagger'}}{q_{\mathrm{A}}q_{\mathrm{B}}}\exp[-\frac{\epsilon^*}{k_{\mathrm{B}}T}], \tag{3.15}$$

$$k' = \frac{RT}{h}\frac{q^{\ddagger'}}{q_{\mathrm{A}}q_{\mathrm{B}}}\exp[-\frac{E^*}{RT}], \tag{3.16}$$

$$q^{\ddagger'} = \frac{Z_{\mathrm{t}}^{\ddagger}}{V}Z_{\mathrm{r}}^{\ddagger}Z_{\mathrm{v}}^{\ddagger'}Z_{\mathrm{e}}^{\ddagger}, \tag{3.17}$$

$$q^{\mathrm{F}} = \frac{Z_{\mathrm{t}}^{\mathrm{F}}}{V}Z_{\mathrm{e}}^{\mathrm{F}}, \tag{3.18}$$

$$q^{\mathrm{H_2}} = \frac{Z_{\mathrm{t}}^{\mathrm{H_2}}}{V}Z_{\mathrm{r}}^{\mathrm{H_2}}Z_{\mathrm{v}}^{\mathrm{H_2}}Z_{\mathrm{e}}^{\mathrm{H_2}}, \tag{3.19}$$

$$\frac{q^{\ddagger'}}{q^{\mathrm{F}}q^{\mathrm{H_2}}} = Q_{\mathrm{t}}Q_{\mathrm{r}}Q'_{\mathrm{v}}Q_{\mathrm{e}}, \tag{3.20}$$

$$Q_{\mathrm{t}} = \frac{\frac{(2\pi m^{\ddagger}k_{\mathrm{B}}T)^{3/2}}{h^3}}{\frac{(2\pi m^{\mathrm{F}}k_{\mathrm{B}}T)^{3/2}}{h^3}\frac{(2\pi m^{\mathrm{H_2}}k_{\mathrm{B}}T)^{3/2}}{h^3}} = 4.2494\mathrm{e}-31, \tag{3.21}$$

$$Q_{\mathrm{r}} = \frac{\frac{8\pi^2 I^{\ddagger}k_{\mathrm{B}}T}{h^2}}{\frac{8\pi^2 I^{\mathrm{H_2}}k_{\mathrm{B}}T}{2h^2}} = 32.3043, \tag{3.22}$$

$$Q'_{\mathrm{v}} = \prod\frac{1}{1-\exp[-\frac{h\nu}{k_{\mathrm{B}}T}]} = 1.3748, \tag{3.23}$$

$$Q_{\mathrm{e}} = \frac{4}{1\times 4} = 1, \tag{3.24}$$

$$k = 8.1650\mathrm{e}-18, \tag{3.25}$$

$$k' = 4917060. \tag{3.26}$$

3.5. 3.14.

$$Q_{\mathrm{t}} \propto \prod T^{3/2}, \tag{3.27}$$

$$Q_{\mathrm{r}} \propto \prod\begin{cases} T, & \text{linear} \\ T^{3/2}, & \text{nonlinear}\end{cases} \tag{3.28}$$

$$\frac{1}{1-\exp[-\frac{h\nu}{k_{\mathrm{B}}T}]} \sim \frac{k_{\mathrm{B}}T}{h\nu} \implies \tag{3.29}$$

$$Q'_{\mathrm{v}} \propto \prod T, \tag{3.30}$$

$$Q_{\mathrm{e}} \propto T^0, \tag{3.31}$$

$$A \propto TQ_{\mathrm{t}}Q_{\mathrm{r}}Q'_{\mathrm{v}}Q_{\mathrm{e}}, \tag{3.32}$$

a.

$$\log_T A \propto 1 + (-\frac{3}{2}) + (0) + (3 - 1) = \frac{3}{2} = n, \tag{3.33}$$

b.

$$\log_T A \propto 1 - \frac{3}{2} + \frac{3}{2} - 2 + 5 - 2 = 2 = n, \tag{3.34}$$

c.

$$\log_T A \propto 1 - \frac{3}{2} - \frac{3}{2} + 17 - 12 = 3 = n. \tag{3.35}$$

4. 第五章作业

4.1. 5.1.

$$
\begin{aligned}
k &= 4\pi(D_\mathrm{A}+D_\mathrm{B})(r_\mathrm{A}+r_\mathrm{B}) && (4.1)\\
&= 4\pi\frac{k_\mathrm{B}T}{6\pi\eta}\frac{(r_\mathrm{A}+r_\mathrm{B})^2}{r_\mathrm{A}r_\mathrm{B}} && (4.2)\\
&= \frac{8k_\mathrm{B}T}{3\eta}, && (4.3)
\end{aligned}
$$

depends no size.

4.2. 5.3.

$$
\begin{aligned}
&\frac{\mathrm{d}x}{\mathrm{d}t} = k_f[\mathrm{A}][\mathrm{B}] - k_r[\mathrm{C}] = k_f([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x) - k_r([\mathrm{C}]_0 + x), && (4.4)\\
&k_f[\mathrm{A}]_e[\mathrm{B}]_e = k_r[\mathrm{C}]_e, && (4.5)\\
&k_f(x_e - x + A_e)(x_e - x + B_e) - k_r(C_e - x_e + x) = && (4.6)\\
&k_f(x_e - x)((x_e - x) + A_e + B_e) + k_r(x_e - x), && (4.7)\\
&-\frac{\mathrm{d}y}{\mathrm{d}t} = k_f y(y + A_e + B_e) + k_r y, && (4.8)\\
&\frac{1}{y(k_r + k_f(y + A_e + B_e))}\,\mathrm{d}y = -\,\mathrm{d}t, && (4.9)\\
&(\frac{1}{y} - \frac{k_f}{k_r + k_f(y + A_e + B_e)})\,\mathrm{d}y = -(k_r + k_f(A_e + B_e))\,\mathrm{d}t, && (4.10)\\
&\ln\frac{y_t}{y_0} - \ln\frac{k_r + k_f(y_t + A_e + B_e)}{k_r + k_f(y_0 + A_e + B_e)} = -(k_r + k_f(A_e + B_e))t, && (4.11)\\
&\ln\frac{x_e - x_t}{x_e}. && (4.12)
\end{aligned}
$$

$$
\begin{aligned}
&y^2 \ll y \implies && (4.13)\\
&-\frac{\mathrm{d}y}{\mathrm{d}t} = k_f y(A_e + B_e) + k_r y, && (4.14)\\
&\frac{1}{y(k_r + k_f(A_e + B_e))}\,\mathrm{d}y = -\,\mathrm{d}t, && (4.15)\\
&\ln\frac{y_t}{y_0} = -(k_r + k_f(A_e + B_e))t, && (4.16)
\end{aligned}
$$

$$
\begin{aligned}
&x_e - x = x_e \exp[-(k_r + k_f(A_e + B_e))t], && (4.17)\\
&\ln\frac{x_e - x}{x_e} = -(k_r + k_f(A_e + B_e))t, && (4.18)
\end{aligned}
$$

4.3. 5.4.

$$\ln k \sim \sqrt{I}: \tag{4.19}$$

$$r_1 = 0.9579, r_2 = 0.9947. \tag{4.20}$$

$$k_2 = -1.64, \tag{4.21}$$

4.4. 5.5.

$$k = 4\pi 2D_{\mathrm{I}}2r_{\mathrm{I}} = 4.8\pi\mathrm{e} - 18, \tag{4.22}$$

$$k' = N_{\mathrm{A}}k = 9.08\mathrm{e}+9\mathrm{M}^{-1}\mathrm{s}^{-1} > 8.2\mathrm{e}+9. \tag{4.23}$$

4.5. 5.6.

$$r = k[\mathrm{ABC}^{\ddagger}] = k_2\frac{\gamma^{\mathrm{A}}\gamma^{\mathrm{B}}\gamma^{\mathrm{C}}}{\gamma^{\ddagger}}K^{\ddagger}[\mathrm{A}][\mathrm{B}][\mathrm{C}], \tag{4.24}$$

$$k_0 = k[\gamma \equiv 1], \tag{4.25}$$

$$k = k_0\frac{\gamma^{\mathrm{A}}\gamma^{\mathrm{B}}\gamma^{\mathrm{C}}}{\gamma^{\ddagger}}, \tag{4.26}$$

$$\lg\gamma^{\mathrm{B}} = -Az_{\mathrm{B}}^2\sqrt{I} \implies \tag{4.27}$$

$$\lg k = \lg k_0 - A\sqrt{I}\left(z_{\mathrm{A}}^2 + z_{\mathrm{B}}^2 + z_{\mathrm{C}}^2 - (z_{\mathrm{A}} + z_{\mathrm{B}} + z_{\mathrm{C}})^2\right) = \lg k_0 + 2A\sqrt{I}\left(z_{\mathrm{A}}z_{\mathrm{B}} + z_{\mathrm{B}}z_{\mathrm{C}} + z_{\mathrm{C}}z_{\mathrm{A}}\right). \tag{4.28}$$