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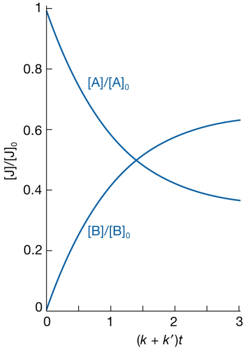

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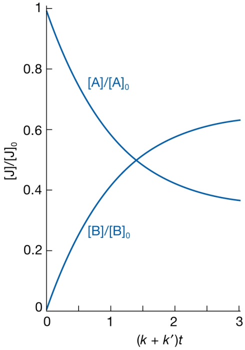

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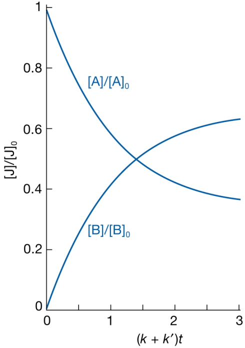

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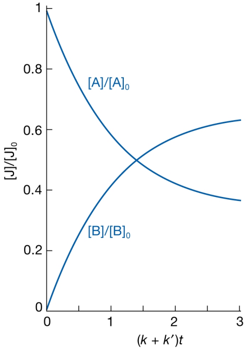

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more generally, $K = \frac{k_a}{k'_a} \cdot \frac{k_b}{k'_b} \cdot \frac{k_c}{k'_c} \cdot \cdots$

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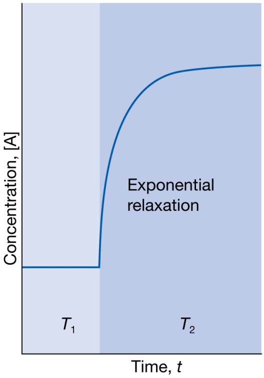

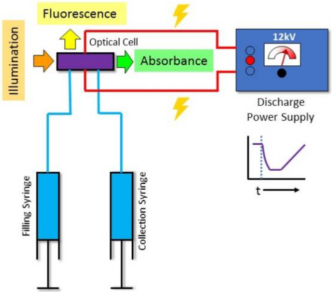

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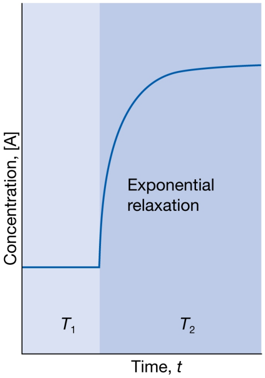

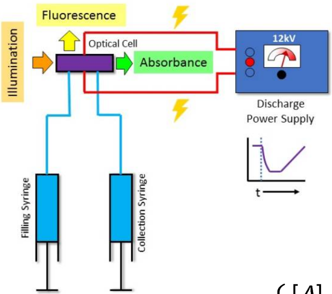

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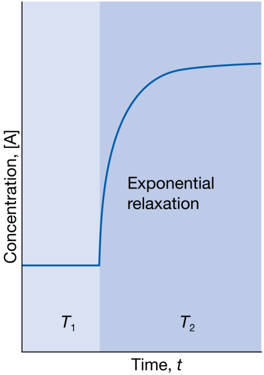

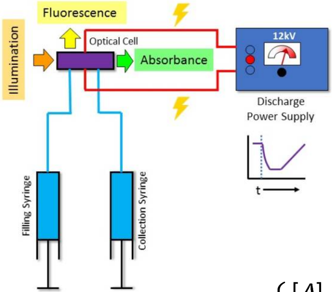

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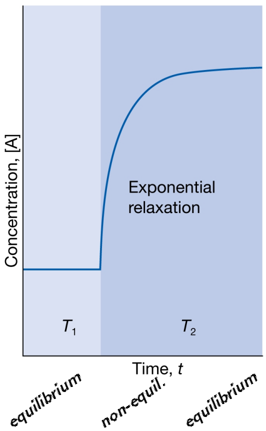

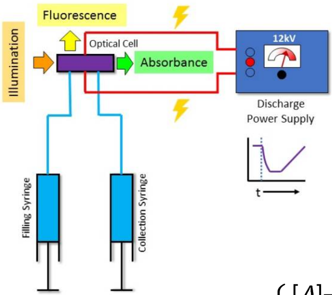

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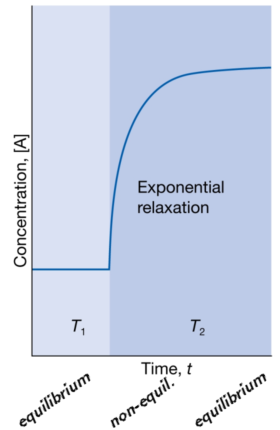

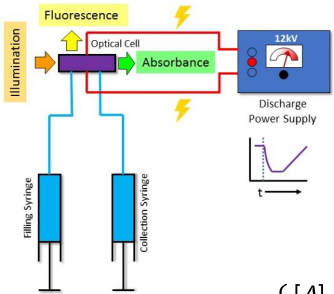

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Some equilibria are also sensitive to pressure : pressure-jump techniques also used

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find $k_2 = 1.4 \times 10^{11}$ dm^{3}mol^{-1}s^{-1} and $k_1 = 2.4 \times 10^{-5}$s^{-1}

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Activation energy:
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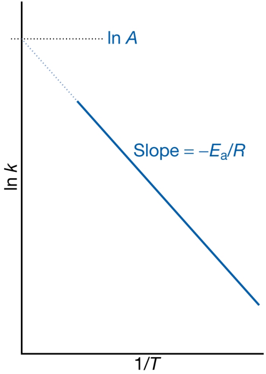
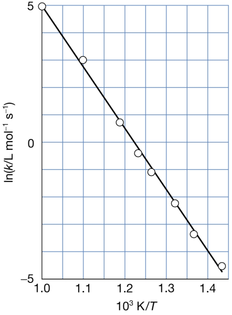


second-order decomposition of acetaldehyde (ethanal, CH_3CHO)

T/K	700	730	760	790	810	840	910	1000
$k/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	0.011	0.035	0.105	0.343	0.789	2.17	20.0	145
$(10^3\,\mathrm{K})/T$	1.43	1.37	1.32	1.27	1.23	1.19	1.10	1.00
$\ln(k/\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	−4.51	−3.35	−2.25	−1.07	−0.24	0.77	3.00	4.98



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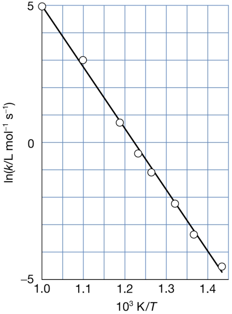

slope=-22.7

intercept=27.7 $\Longrightarrow$ $E_a = 22.7 \times 8.3145 \mathrm{JK^{-1} mol^{-1}} \times 10^3 \mathrm{K}$

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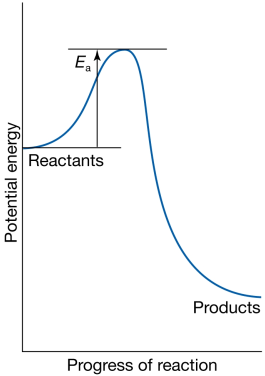
- negative activation energy $\Longrightarrow$ rate decreases as temperature is raised
- $\boxed{E_a = RT^2 \left(\frac{d \ln k}{dT}\right)}$

Potential energy profile for exothermic reaction



- stronger temperature dependence of rate constant (steeper slope) $\Longrightarrow$ higher activation energy
- high activation energy $\Longrightarrow$ rate constant depends strongly on temperature.
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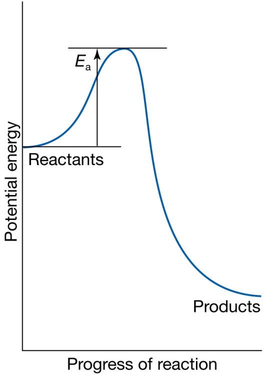

activated complex
versus
transition state

Effect of catalyst

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(2) & (5)

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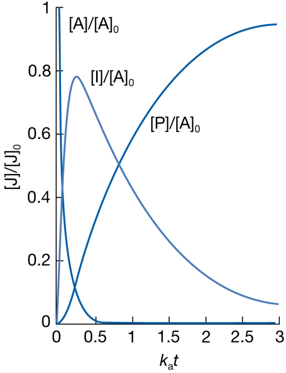
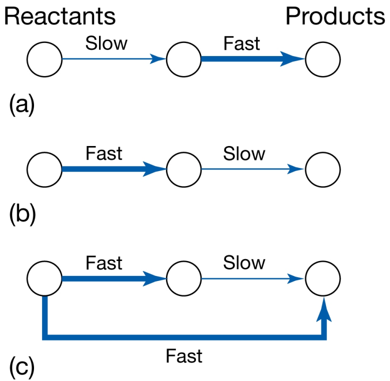
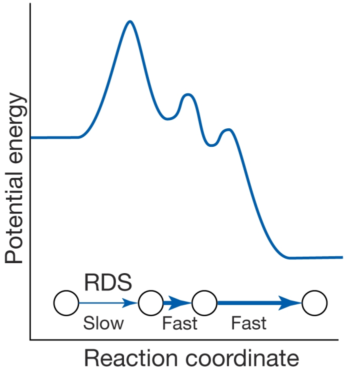
$$\implies [I] = \frac{k_a}{k_b - k_a}\left(e^{-k_a t} - e^{-k_b t}\right)[A]_0$$



$k_a = 10k_b$





slow step is rate determining [not in (c)] steady state approximation: $\frac{d[\mathsf{I}]}{dt} = 0$

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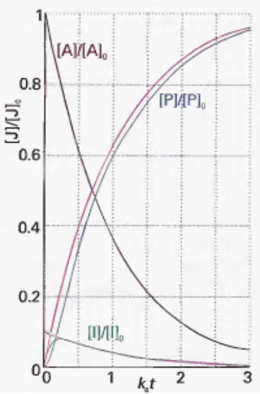
The concentrations of the intermediates remains small and hardly changes during reaction.

$\implies \frac{k_a}{k_b} \ll 1$

$\implies \frac{d[P]}{dt} = k_b[I] = k_a[A]$

$\implies [P] = \left(1 - e^{-k_a t}\right)[A]_0$



$k_b = 20k_a$

exact (black) versus s.s. (red)

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rate law?

Identified intermediates: NO and NO_3

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and the rate of decomposition of N_2O_5:
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$$= -k_a[N_2O_5] + k_a'\frac{k_a[N_2O_5]}{k_a'+k_b} - k_b\frac{k_a[N_2O_5]}{k_a'+k_b} = -\frac{2k_ak_b[N_2O_5]}{k_a'+k_b}$$

Kinetic and thermodynamic control

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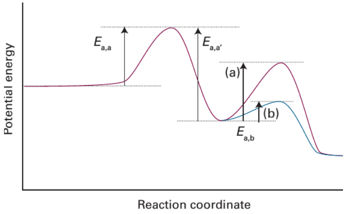

3 activation energies to take into account:

two referring to reversible steps of pre-equilibrium and one for final step

relative magnitudes of activation energies determine

overall activation energy (a) > 0 or (b) < 0

If we include the details:

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same as before for $k_a' \gg k_b$