4. Studying Dynamic Processes by NMR

- **Intramolecular processes**
  - rotations (M-C, M-M, C-C or other bonds)
  - skeletal rearrangements
  - ring whizzing (migration of metal on $\eta^1$-$C_5H_5$ rings)
  - hapticity changes ($\eta^1 \rightarrow \eta^3$)
  - bridge-terminal exchange (eg. CO complexes)

- **Intermolecular processes**
  - Ligand exchange (dissociation / re-association):
    - $J_{XY}$ coupling *completely lost* if the X-Y bond breaks
    - $J_{XY}$ coupling *averaged* if X-Y bond retained
But...how do we know a dynamic process is operative?

- broadened lines
- temperature dependence
- field dependence
- spectra that are too simple or too complicated for expected structure

What we see in the spectrum of a dynamic system depends on the particular dynamic process involved and the rate constants associated with it, the temperature and the magnetic field of the NMR instrument.
However, for any process there are three distinct temperature regimes:

**Slow exchange (Fig 1a)** \( T < T_c \quad k << \delta \nu \)
- distinct resonances are observed for the exchanging partners

**Coalescence (Fig 1c)** \( T = T_c \quad k \approx \delta \nu \)
- exchanging resonances just merge into a single broad peak

**Fast exchange (Fig 1e)** \( T > T_c \quad k >> \delta \nu \)
- a weighted average signal is observed for the exchanging resonances

where \( T_c = \text{coalescence T} \), \( k \) is the rate constant and \( \delta \nu \) is the separation of the exchanging resonances at the low T limit in Hz.
Figure 1 Axial-equatorial exchange in cyclohexane-d_{11}
Extraction of rate data from the spectra: equal population, 2-site exchange

**Note:** For a simple *equal-population, 2-site* exchange process like that in Fig. 1, there are straightforward mathematical formulas linking $\delta \nu$ and **line widths** to $k$. In any other situation the extraction of rate data is more complex and usually requires computer simulation.

**Slow exchange regime:** $k = \pi (w - w_0)$
- where $w_0$ is the width at half height of the peak at the low $T$ limit (0.4 Hz in Fig 1a) and $w$ is the width of the peak at the $T$ in question (2.4 Hz)

**At coalescence:** $k = \pi (\delta \nu (2)^{-1/2})$
- where $\delta \nu$ is the chemical shift difference between the resonances in the low $T$ limit (29 Hz in Fig 1a)

**Fast exchange regime:** $k = \pi (\delta \nu)^2 (w - w_f)^{-1} (2)^{-1/2}$
- where $w$ is the width of the resonance at $T$ (eg. 2.8 Hz in Fig 1d) and $w_f$ is the width of the resonance at the fast exchange limit (0.5 Hz in Fig 1e)
Calculating activation parameters from rate data:

**Eyring equation:**

\[ k = (k_b T/h)e^{-\Delta G^*/RT} \]

therefore

\[ \Delta G^* = -RT[\ln(k/T) + \ln(h/k_b)] \]

and

\[ k = (k_b T/h)e^{-\Delta H^*/RT}e^{\Delta S^*/R} \]

more usefully:

\[ \ln(k/T) = -\Delta H^*/RT + [\Delta S^*/R - \ln(h/k_b)] \]

so a plot of \( \ln(k/T) \) versus \( 1/T \) is a **straight line** for which:

\[ \Delta H^* = -(\text{slope})R \]

and

\[ \Delta S^* = [\text{intercept} + \ln(h/k_b)]R \]

\( \Delta G^* \) can be obtained directly at the coalescence temperature \( T_c \) using the formula given below:

\[ \Delta G^* = (1.912 \times 10^{-2})(T_c)[9.972 + \log(T_c/\delta v)] \]

in kJ/mol

where \( T_c \) is in K and \( \delta v \) is in Hz
For the example in Fig 1, the following rates can be calculated using the appropriate formula:

\[ k_{-78} = \pi(2.4-0.4) = 6.28 \text{ s}^{-1} \]

\[ k_{-61} = \pi(29)(2)^{-1/2} = 64 \text{ s}^{-1} \text{ (coalescence temperature)} \]

\[ k_{-43} = \pi(29)^2/(2)(2.8-0.5) = 566 \text{ s}^{-1} \]

From the Eyring plot:

\[ \Delta H^* = -5556 \text{ K} \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1})/1000 = 46 \text{ kJ/mol} \]

\[ \Delta S^* = [25.06 + \ln(h/k_b)]*8.314 = (25.06-23.76)*8.314 = 11 \text{ J K}^{-1} \text{ mol}^{-1} \]
Significance of $\Delta S^*$

- **Large positive values = less ordered transition state**
  - consistent with processes like ligand dissociation or bond breaking

- **Large negative values = more ordered transition state**
  - consistent with associative processes and bond making steps
  - also expected for highly ordered transition states such as a four-membered transition state

$\sigma$-bond metathesis

However, getting reliable values of $\Delta S^*$ requires many recording the NMR at a large number of temperatures because the error associated with the Eyring plot is large.
Organometallic examples:

a) restricted rotation about a bond
b) exchange with free ligand

Ethylene exchange with a titanacyclopentane

Figure 1. $^1$H NMR (200 MHz) spectra of [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_2$)$_4$] (4) and ethylene in C$_6$D$_5$CD$_3$ solvent (* indicates protio impurity) over the temperature range $-30$ to $+60$ °C.
Scheme 4