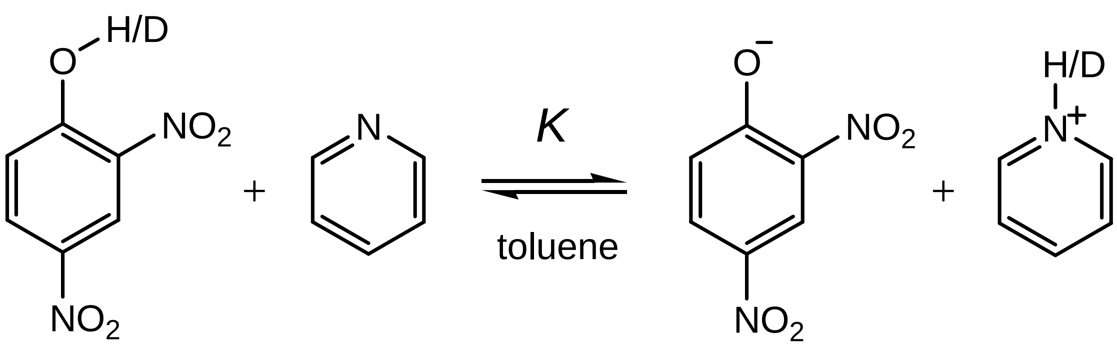
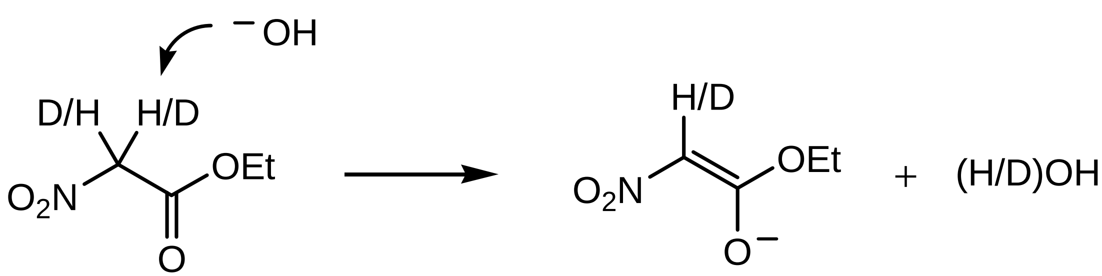
Isotope Effects

Remarkably, replacing one isotope of an atom with another can substantially affect reaction equilibria and rates.



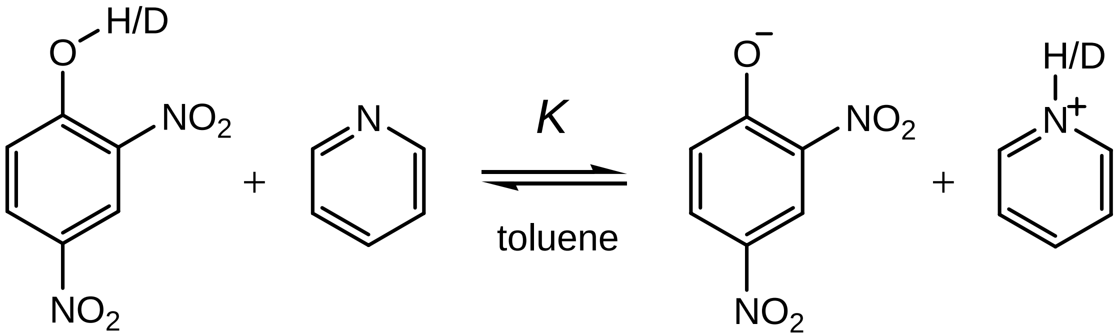
$$\frac{K_H}{K_D} = 1.4$$



$$\frac{k_H}{k_D} = 4.6$$

Just replacing H with D makes reaction go 5 times slower!

Equilibrium Isotope Effects



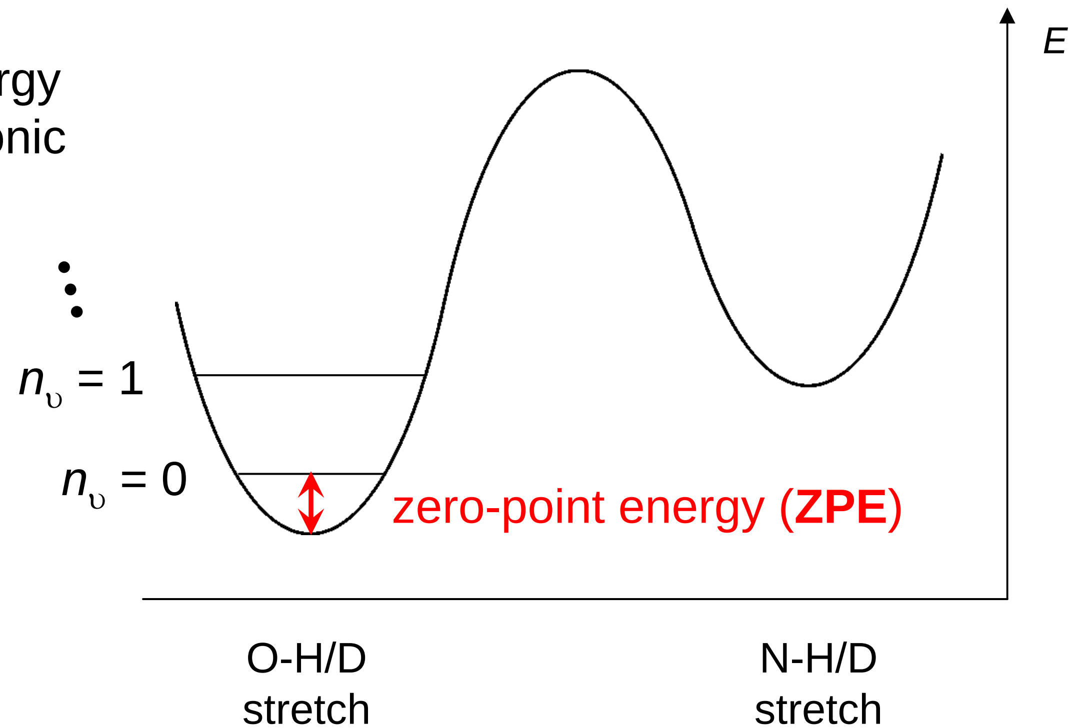
$$\frac{K_H}{K_D} = 1.4$$

Each side of potential energy diagram represents harmonic vibrational potential well.

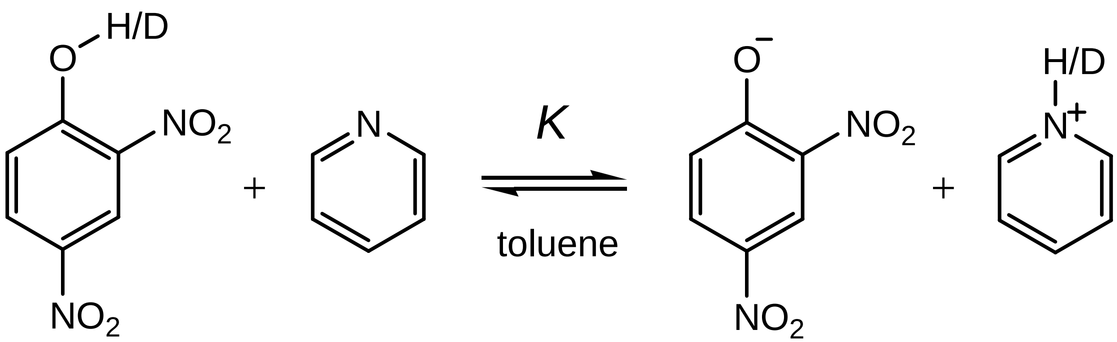
Vibrational states have energy

$$E = (n_\upsilon + ½)h\nu$$

$$\textbf{ZPE} = \frac{1}{2}h\nu$$



Equilibrium Isotope Effects

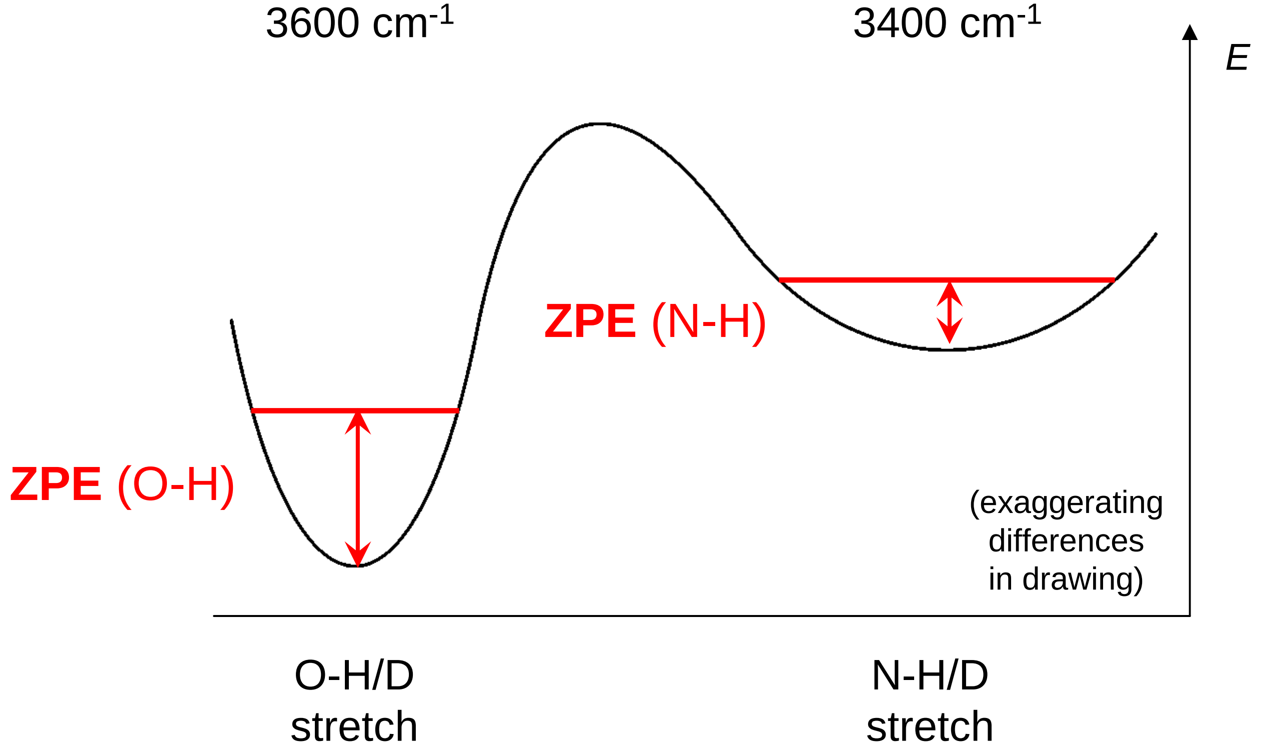


$$\frac{K_H}{K_D} = 1.4$$

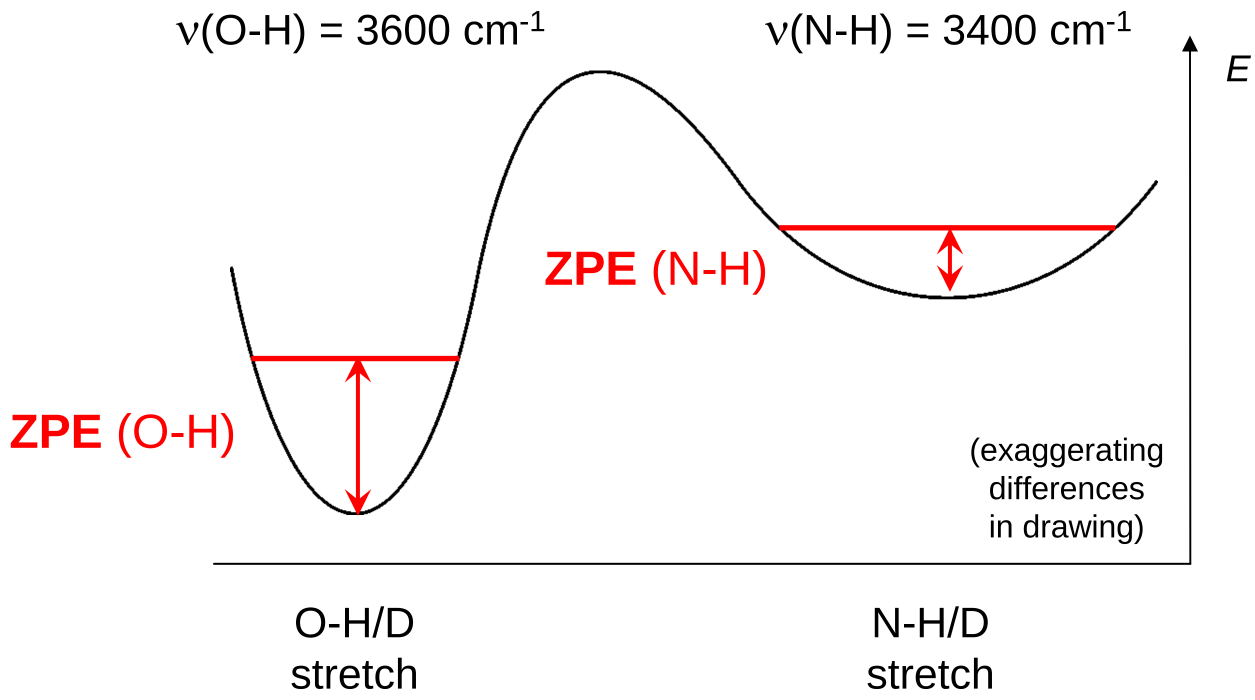
ν(O-H) = 3600 cm^{-1}

ν(N-H) = 3400 cm^{-1}

ZPE = $\frac{1}{2}h\nu$

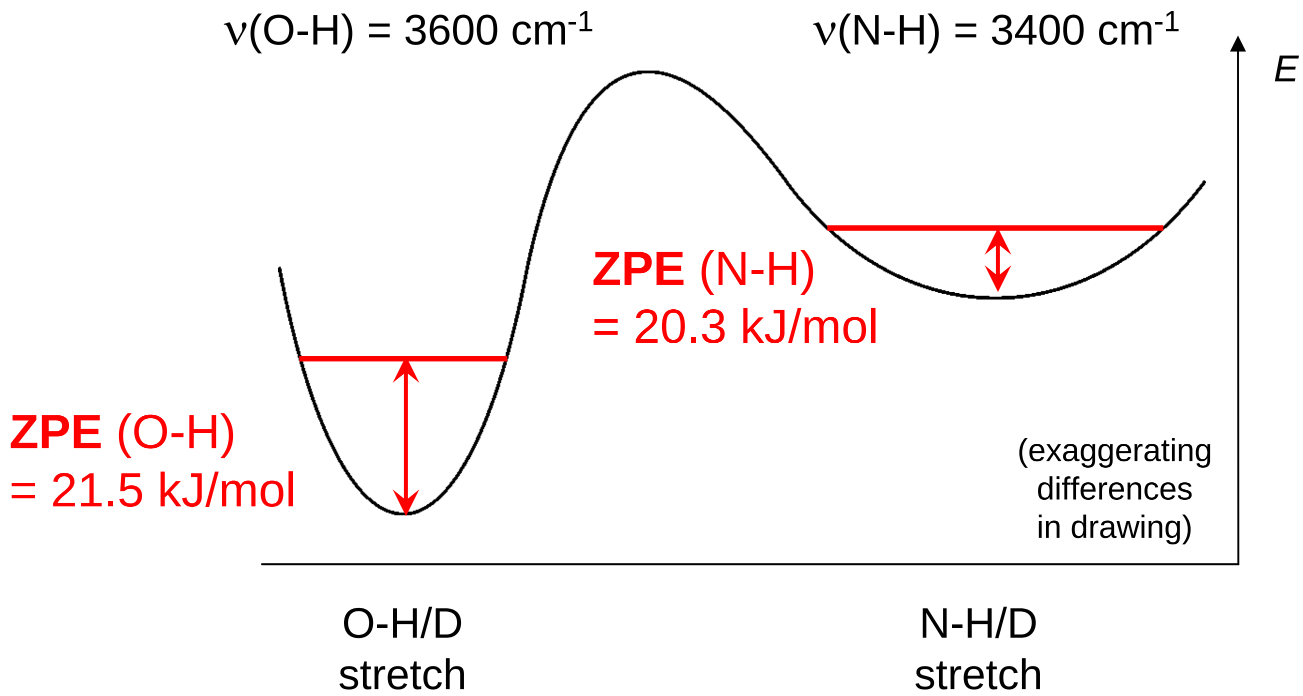


$$\mathbf{ZPE} = \frac{1}{2} h\nu$$



[redacted]

$$\textbf{ZPE} = \frac{1}{2} h\nu$$



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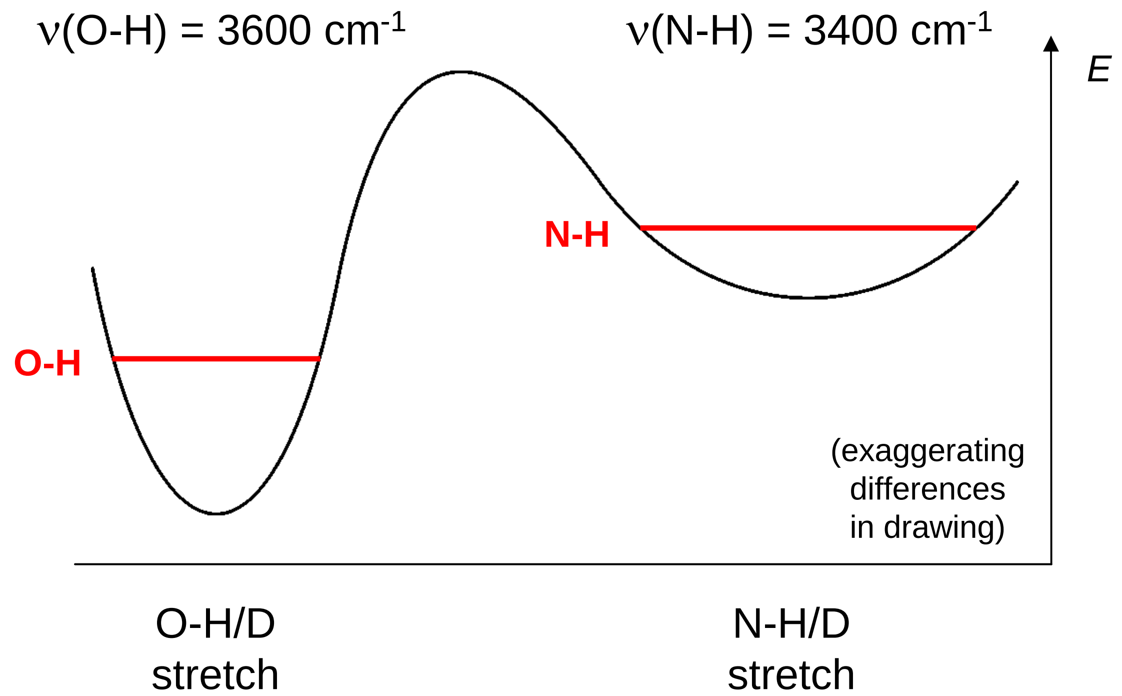
On this diagram, where do O-D and N-D appear?



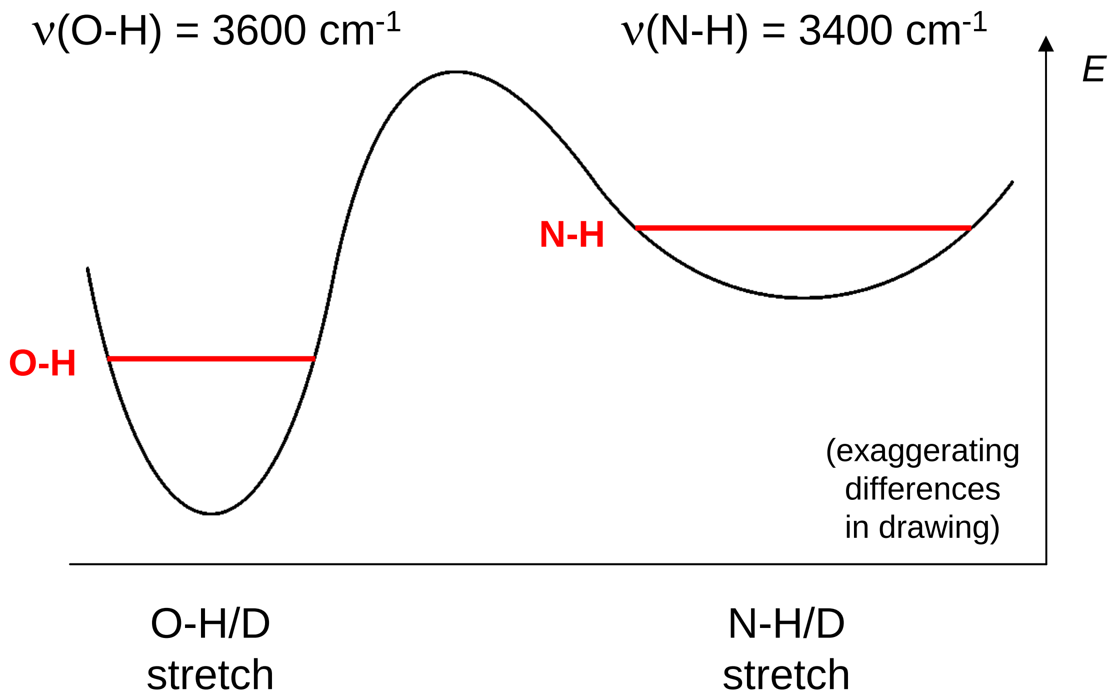
[redacted]

Don't know ν for O-D or N-D, but Hooke's Law says:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

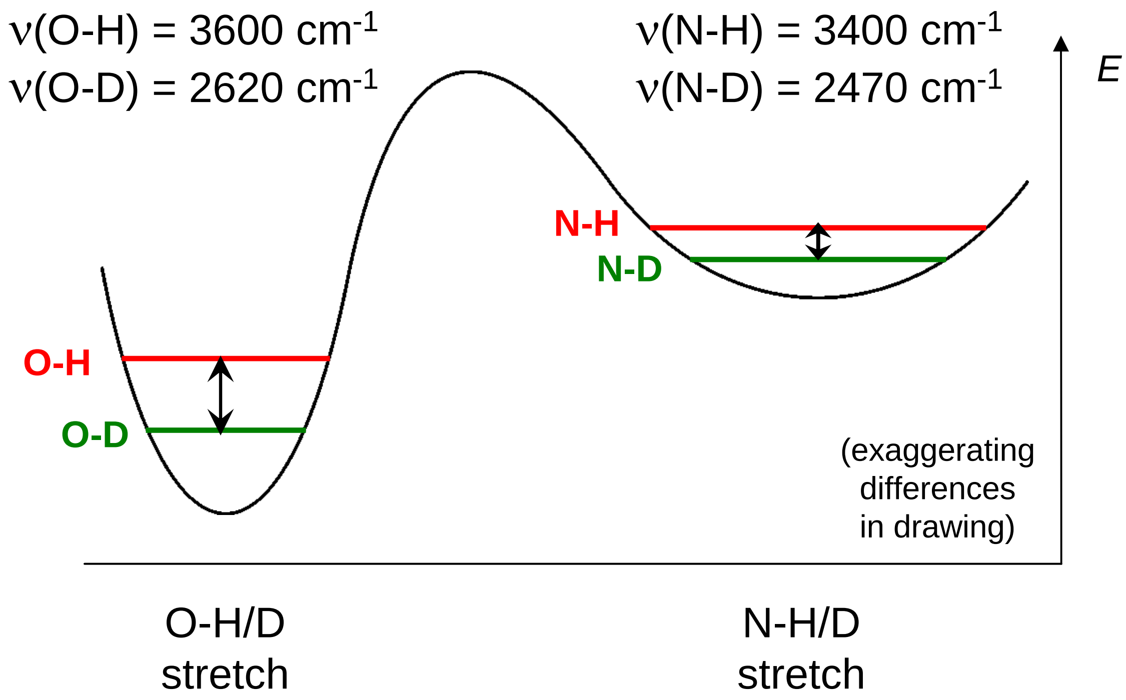
Hooke's force constant (k)

reduced mass, $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$



[redacted]

So, higher-frequency bond has narrower well, higher energies and larger energy differences.



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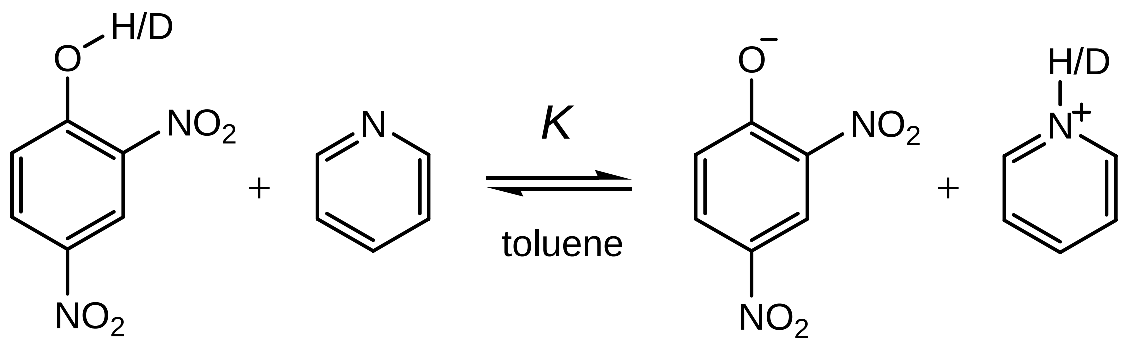
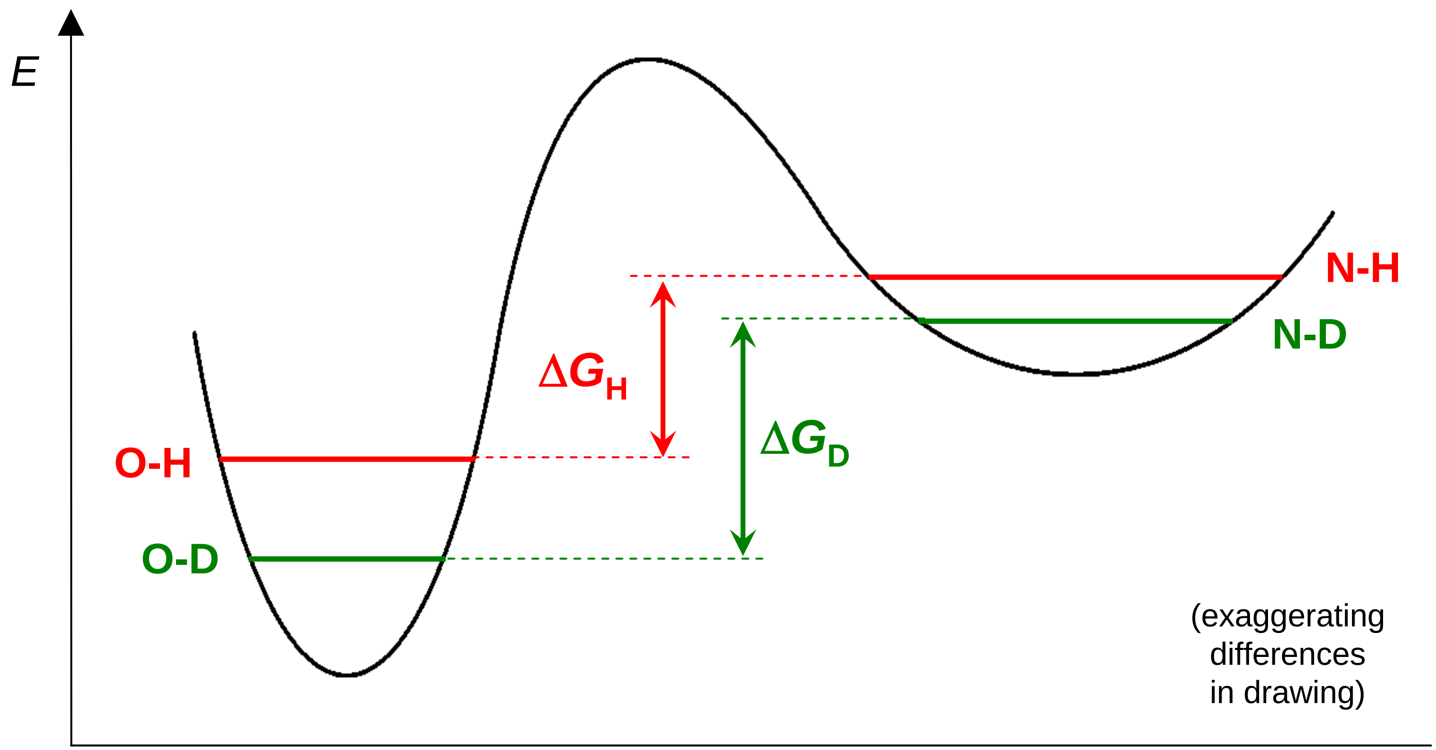
Equilibrium Isotope Effects





$\Delta G_H < \Delta G_D$

$K_H > K_D$

$$\frac{K_H}{K_D} > 1$$

(= 1.14
here)