Introduction of Statistical Thermodynamic Calculations

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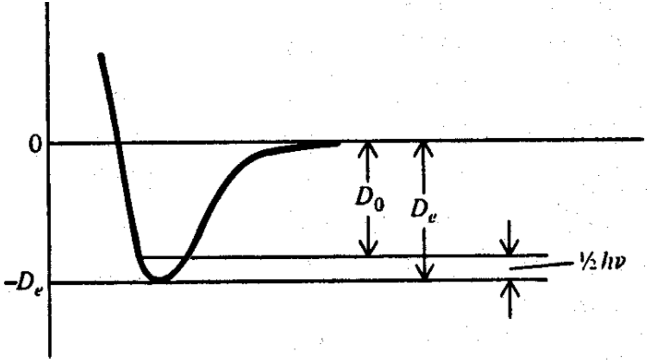
Mar 30, 2026

Ideal Diatomic Gases

- Potential energy from Schrödinger equation
  - Must be approximated for more complicated molecules (all atoms larger than H)
  - Born-Oppenheimer approximation: atomic nuclei assumed to be fixed
  - D_0 and v: from experimental data
  - $u_e(r)$ similar to van der Waals interaction curve, but much deeper (~100 kcal/mol, bond energy)



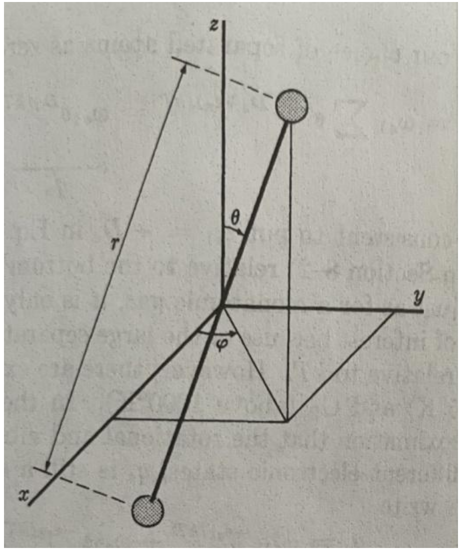
Degrees of Freedom

- Consider molecule in a volume *V*
- Variables
  - Translation: *x*, *y*, *z*; Rotation: *ϑ*, *φ*; Vibration: *r*
  - 6 degrees of freedom (might be reduced)

$$H = H_t + H_r + H_v + H_e$$

$$\epsilon = \epsilon_t + \epsilon_r + \epsilon_v + \epsilon_e$$

$$Q = \frac{1}{N!} q^N \qquad q(V,T) = q_t(V,T) q_r(T) q_v(T) q_e(T)$$



Partition Functions

- Transition & electron
  - Only ground state matters for most cases

$$q_t = \int_0^\infty \omega(\epsilon) e^{-\epsilon/kT} \mathrm{d}\epsilon = \frac{\pi}{4} \left[\frac{8(m_1+m_2)kT}{h^2}\right]^{3/2} V \int_0^\infty u^{1/2} e^{-u} \mathrm{d}u$$
$$= \left[\frac{2\pi(m_1+m_2)kT}{h^2}\right]^{3/2} V$$

$$q_e q_v = \omega_{e1} \sum_n e^{-(-D_e+\epsilon_n)/kT} = \underbrace{\omega_{e1} e^{D_e/kT}}_{q_e} \underbrace{\sum_n e^{-\epsilon_n/kT}}_{q_v}$$

  - One of the exceptions: NO (> 15K), 2^{nd} energy level considered

$$q_e = \omega_{e1} e^{-\epsilon_{e1}/kT} + \omega_{e2} e^{-\epsilon_{e2}/kT}$$

Partition Functions

- Vibration (Determined by the potential energy)
  - Motion of a 1-D harmonic oscillator

$$u_e(r) = -D_e + \frac{1}{2}f(r-r_e)^2 \qquad \text{where } f = \left(\frac{\mathrm{d}^2 u_e}{\mathrm{d}r^2}\right)_{r=r_e}$$

$$\mu\ddot{x} = -fx \qquad \text{where } x = r - r_e \text{ and } \mu = \frac{m_1 m_2}{m_1 + m_2} \quad \Rightarrow \quad \nu = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}}$$

  - Energy states & Thermodynamic functions:

$$\epsilon_n = \left(n + \frac{1}{2}\right)h\nu \qquad n = 0, 1, 2, \ldots$$

$$q_v = e^{-\Theta_v/2T}\sum_{n=0}^{\infty} e^{-n\Theta_v/T} = \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}} \qquad \text{where } \Theta_v = \frac{h\nu}{k}$$

$$E_v = NkT^2\frac{\mathrm{d}\ln q_v}{\mathrm{d}T} = Nk\left(\frac{\Theta_v}{2} + \frac{\Theta_v}{e^{\Theta_v/T} - 1}\right)$$

$$C_{Vv} = \left(\frac{\partial E_v}{\partial T}\right)_N = Nk\left(\frac{\Theta_v}{T}\right)^2 \frac{e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2}$$

$$w_{n>0} = \sum_{n=1}^{\infty} \frac{e^{-(n+1)\Theta_v/2T}}{q_v} = e^{-\Theta_v/T}$$

Partition Functions

- Rotation

$$\epsilon_j = \frac{J(J+1)h^2}{2I} \qquad J = 0, 1, 2, ...$$

$$q_r = \sum_j \omega_j e^{-\epsilon_j/kT} = \sum_{j=0}^{\infty}(2j+1)e^{-j(j+1)\Theta_r/T}$$

$$\to \int_0^{\infty}(2j+1)e^{-j(j+1)\Theta_r/T}\mathrm{d}j = \int_0^{\infty} e^{-j(j+1)\Theta_r/T}\mathrm{d}[j(j+1)]$$

$$= \frac{T}{\Theta_r} = \frac{8\pi^2 IkT}{h^2} \qquad \text{when } T \gg \Theta_r\text{; otherwise,}$$

$$q_r = \frac{T}{\Theta_r}\left[1 + \frac{1}{3}\left(\frac{\Theta_r}{T}\right) + \frac{1}{15}\left(\frac{\Theta_r}{T}\right)^2 + \frac{4}{315}\left(\frac{\Theta_r}{T}\right)^3 + ...\right]$$

If symmetric: $q_r = \dfrac{T}{2\Theta_r} = \dfrac{4\pi^2 IkT}{h^2}$

Thermodynamic functions:

$$F_r = -NkT\ln\left(\frac{T}{\sigma\Theta_r}\right) \qquad E_r = NkT^2\frac{\mathrm{d}\ln q_r}{\mathrm{d}T} = NkT$$

$$S_r = \frac{E_r - F_r}{T} = Nk\ln\left(\frac{T}{\sigma\Theta_r}\right) \qquad C_{Vr} = \left(\frac{\partial E_r}{\partial T}\right)_N = Nk$$

where $\sigma = 1, 2$ (1 for unsymmetrical, 2 for symmetrical molecules)

Thermodynamic Functions

Magnitude of energy:

$$\Delta\epsilon(\text{translation}) = O(10^{-18}\,\text{eV})$$
$$\Delta\epsilon(\text{rotation}) = O(5\times 10^{-4}\,\text{eV})$$
$$\Delta\epsilon(\text{vibration}) = O(0.3\,\text{eV})$$
$$\Delta\epsilon(\text{electronic}) = O(5\,\text{eV})$$
$$kT(300\,\text{K}) = O(0.03\,\text{eV})$$

Criteria:

Classical: $\Delta\epsilon \ll kT$ $\quad \Theta \ll T$

Quantum: $\Delta\epsilon = O(kT)$ $\quad \Theta = O(T)$

Unexcited: $\Delta\epsilon \gg kT$ $\quad \Theta \gg T$

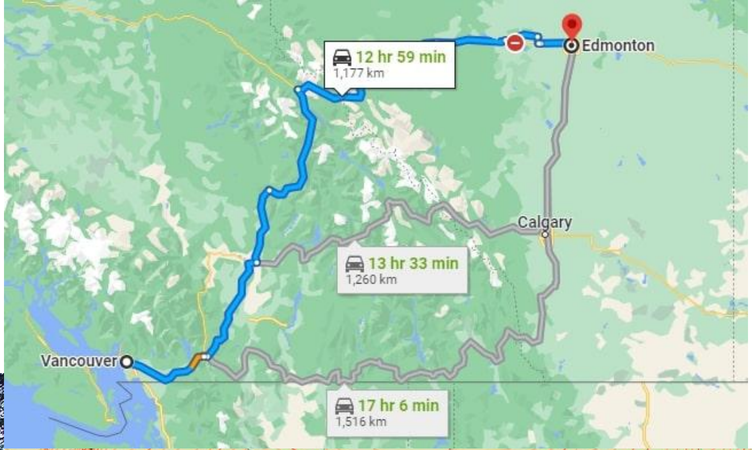
Overall thermodynamic functions:

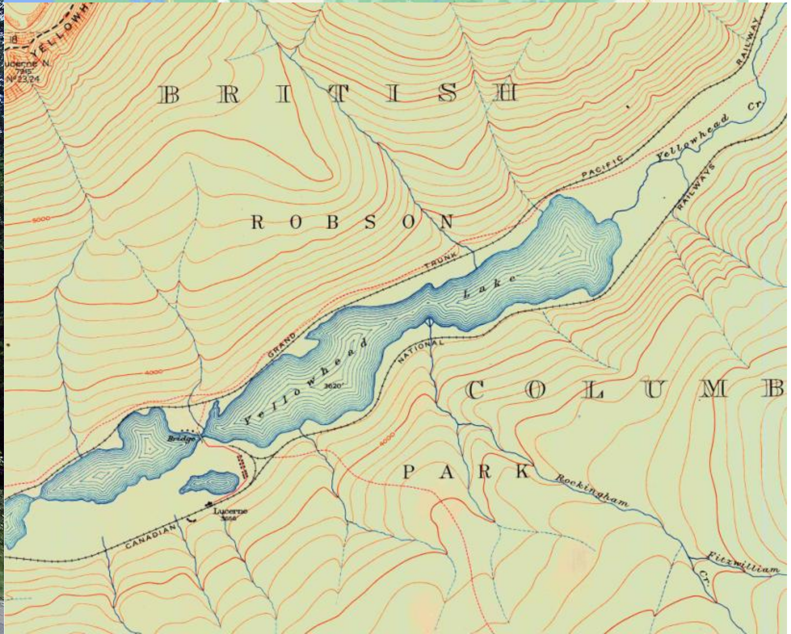
$$F = -kT\ln Q = F_t + F_r + F_v + F_e$$
$$\text{where } F_t = -NkT\ln\left(\frac{q_t e}{N}\right) \text{ and } F_v = -NkT\ln q_v$$
$$\frac{F}{NkT} = -\ln\left[\frac{2\pi(m_1+m_2)kT}{h^2}\right]^{3/2}\frac{Ve}{N} + \ln\frac{8\pi^2 IkT}{\sigma h^2} + \frac{h\nu}{2kT} + \ln(1-e^{-h\nu/kT}) - \frac{D_e}{kT} - \ln\omega_{e1}$$
$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = NkT\left(\frac{\partial \ln q_t}{\partial V}\right)_T = \frac{NkT}{V}$$

$$\frac{E}{NkT} = \frac{3}{2} + \frac{2}{2} + \frac{h\nu}{2kT} + \frac{h\nu/kT}{e^{h\nu/kT}-1} - \frac{D_e}{kT}$$
$$\frac{C_v}{Nk} = \frac{3}{2} + \frac{2}{2} + \left(\frac{h\nu}{kT}\right)^2\frac{e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2}$$
$$\frac{S}{Nk} = \ln\left[\frac{2\pi(m_1+m_2)kT}{h^2}\right]^{3/2}\frac{Ve^{5/2}}{N} + \ln\frac{8\pi^2 IkTe}{\sigma h^2} + \frac{h\nu/kT}{e^{h\nu/kT}-1} - \ln(1-e^{-h\nu/kT}) + \ln\omega_{e1}$$
$$\frac{\mu^0(T)}{kT} = -\ln\left[\frac{2\pi(m_1+m_2)kT}{h^2}\right]^{3/2}kT - \ln\frac{8\pi^2 IkT}{\sigma h^2} + \frac{h\nu}{2kT} + \ln(1-e^{-h\nu/kT}) - \frac{D_e}{kT} - \ln\omega_{e1}$$
$$\frac{G}{NkT} = \frac{F}{NkT} + \frac{pV}{NkT} = \frac{\mu}{kT} = \frac{\mu^0(T)}{kT} + \ln p$$

Case: adsorbed molecule
only the vibrational part

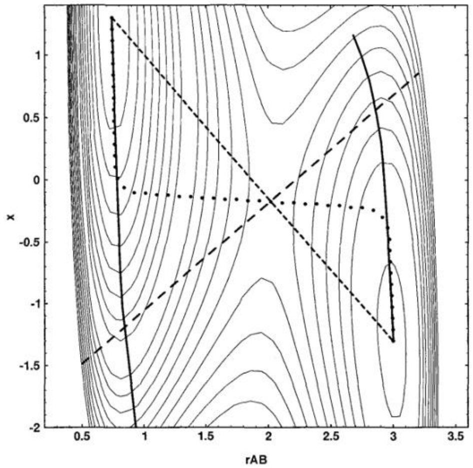
Example:
Edmonton to Vancouver

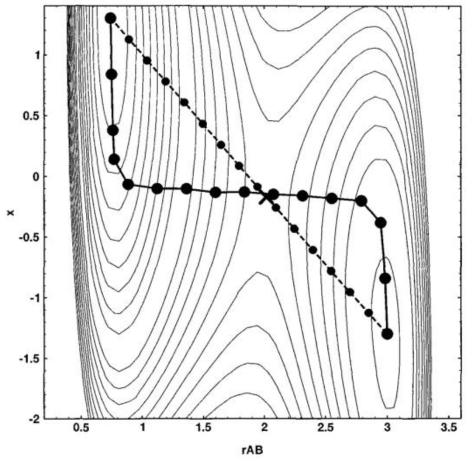




Transition States

- Nudged Elastic Bands (NEB): determine the path of migration





$$F_i = F_i^{V\perp} + F_i^{S\parallel}$$

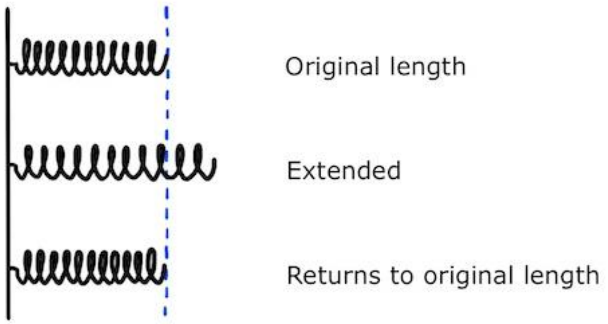
$$\vec{F}_i \;=\; -\vec{\nabla} V(\vec{R}_i) + \vec{F}_i^s$$

$$\vec{F}_i^s \equiv k_{i+1}\left(\vec{R}_{i+1} - \vec{R}_i\right) - k_i\left(\vec{R}_i - \vec{R}_{i-1}\right).$$

- Climbing-Image (CI-NEB): find the maximum (saddle point)

Transition States

- Energy calculation through partition functions
  - Imaginary frequency: one and only one (similar to spring)



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

If k < 0: $\nu \propto \sqrt{-|k|} = i\sqrt{|k|}$

  - Example: O_2 adsorption on W (see supplementary info page 26) https://doi.org/10.1038/s41467-025-63540-w

Thank you