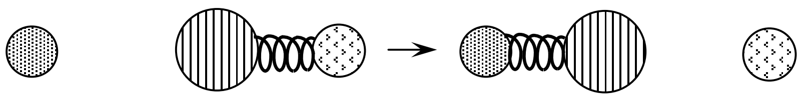
Equilibrium Constants and Statistical Mechanics Example

Example: diatom-atom exchange $A + BC \rightarrow AB + C$ $\Delta E_o = E_o(AB) - E_o(BC)$



A R_{BC}, $\tilde{\nu}_o(BC)$, $D_o(BC)$ R_{AB}, $\tilde{\nu}_o(AB)$, $D_o(AB)$ C

$$K_p = \frac{\left(q^o_{AB}/N_A\right)\left(q^o_C/N_A\right)}{\left(q^o_A/N_A\right)\left(q^o_{BC}/N_A\right)} e^{-\Delta E_o/RT}$$

$$q^o_t = \frac{(2\pi mkT)^{3/2}}{h^3} V^o_m$$

$$q_r = \frac{kT}{\sigma \tilde{B} hc} \qquad \tilde{B} = \frac{\hbar}{4\pi \mu R^2_{AB}\, c}$$

$$q_\nu = \frac{1}{1 - e^{-h\nu_o/kT}} = \frac{1}{1 - e^{-h\tilde{\nu}_o c/kT}}$$

$$K_p = \left(\frac{m_{AB}\, m_C}{m_A\, m_{BC}}\right)^{3/2} \left(\frac{\frac{1}{\sigma \tilde{B}_{AB}}}{\frac{1}{\sigma \tilde{B}_{BC}}}\right) \left(\frac{\frac{1}{1-e^{-h\tilde{\nu}_o(AB)\, c/kT}}}{\frac{1}{1-e^{-h\tilde{\nu}_o(BC)\, c/kT}}}\right) \left(\frac{g_{AB}\, g_C}{g_A\, g_{BC}}\right) e^{-\Delta E_o/RT}$$

$$\left(\frac{1/\tilde{B}_{AB}}{1/\tilde{B}_{BC}}\right) = \frac{\mu_{AB} R^2_{AB}}{\mu_{BC} R^2_{BC}}$$

calculate R_{AB}, $\tilde{\nu}_o(AB)$, and $E_o(AB)$ from MO theory

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from spectroscopic data: since D_o (spectroscopic) $= -E_o$ with $D_o > 0$

$\Delta E_o = [-D_o(AB)] - [-D_o(BC)]$