Cancellation of temperature correction terms

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

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Ideal polyatomic gas

E → Internal Energy

$$\overset{U}{\frac{E}{N}} = \overset{\text{trans}}{\frac{3}{2}kT} + \overset{\text{rot}}{\frac{3}{2}kT} + \sum_{i=1}^{3N-6}\left(\overset{\text{ZPE}}{\frac{h\nu_i}{2}} + \overset{\text{vib}}{\frac{h\nu_i}{e^{h\nu_i/kT}-1}}\right) - \overset{\text{DFT}}{D_e}$$

$$H = E + PV = E + kT$$

$$\frac{H}{N} = \underbrace{\frac{3}{2}kT + \frac{5}{2}kT + \sum_{i=1}^{3N-6}\frac{h\nu_i}{e^{h\nu_i/kT}-1}}_{\text{Temperature corrections}} + \underbrace{\sum_{i=1}^{3N-6}\frac{h\nu_i}{2} - D_e}_{\text{DFT energy + ZPE}}$$

$$\frac{TS}{N} = \frac{5}{2}kT + \overset{\text{translational}}{\ln\left[\frac{2\pi\left(\sum_i m_i\right)kT}{h^2}\right]^{3/2}\frac{V}{N}} + \frac{3}{2}kT + \overset{\text{rot}}{\ln\frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\theta_A\theta_B\theta_C}\right)^{1/2}}$$

$$+ \sum_{i=1}^{3n-6}\frac{h\nu_i}{e^{h\nu_i/kT}-1}\overset{\text{T corr. for vib entropy}}{} - kT\ln\left(1-e^{-h\nu_i/kT}\right)$$

$$= \underbrace{\frac{5}{2}kT + \frac{3}{2}kT + \sum_{i=1}^{3n-6}\frac{h\nu_i}{e^{h\nu_i/kT}-1}}_{\text{Temperature correction}} + \underbrace{\qquad\qquad}_{\text{entropy calculated as } -kT\ln Q}$$

↳ partition function

$$\frac{G}{N} = \frac{H}{N} - \frac{TS}{N} = (\text{DFT energy} + \text{ZPE}) - kT\ln Q$$

$$E^\circ \quad - \quad TS^\circ$$ → common language

$$\boxed{\text{Temperature corrections get cancelled}}$$

A, B, C $\rightarrow$ $\boxed{\text{2-D ideal gas.}}$

$$A^* + B^* \longrightarrow C^*$$

$\rightarrow$ for chemical equilibrium, $\boxed{\sum \mu_i \nu_i = 0}$.

$$\mu_C - \mu_A - \mu_B = 0.$$

A, B, C ideal gas mixture

hence μ_i can calculated separately.

$$\mu_i = -KT\left(\frac{\partial \ln Q}{\partial N_i}\right)_{N_j, V, T}$$

$$Q_i = \frac{q_i^{N_i}}{N_i!} \qquad \mu_i = KT \ln \frac{N_i}{q_i}$$

$$q_{ads_i} = q_{trans}\, q_{rot}\, q_{vib} \cdot \underset{\exp,}{q_e} \left({}^{-E_{bind}}/_{KT} \right)$$

$$q_{trans} = \frac{2\pi m_i KT}{h^2} \cdot A$$

$$\mu_i = KT \cdot \ln \frac{N_i}{\frac{2\pi m_i KT}{h^2} \cdot A \cdot q_{rot}\, q_{vib} \exp\left(\frac{-E_{bind}}{KT}\right)}.$$

$$= -KT \ln \frac{2\pi m_i KT}{h^2} A - KT \ln q_{rot}\, q_{vib} + E_{bind_i} + KT \ln N_i$$

Write every thing in terms of coverage,

hence add & subtract $\ln M$.

(or)

$$= -KT \ln \frac{2\pi m_i KT}{h^2} - KT \ln q_{rot}\, q_{vib} + E_{bind,i} + KT \ln {}^{N_i}/_{A} \cdot \frac{A}{N_i^{\circ}}$$

Normalizing using standard coverage

#

$$= -KT \ln \frac{2\pi m_i KT}{h^2}\left(\frac{A}{N_i}\right)^{\circ} - KT \ln q_{rot}\, q_{vib} + E_{bind,i} + KT \ln \frac{{}^{N}/_{A}}{\left({}^{N_i}/_{A}\right)^{\circ}}$$

choose $\left(\frac{N_i}{A}\right)^0 = \frac{M}{A}$.

$$\mu_i = -KT \ln \frac{2\pi m_i KT}{h^2} \frac{A}{M} - KT \ln q_{rot}\, q_{vib} + E_{bnd,i} + KT \ln \theta_i$$

$$\mu_C - \mu_B - \mu_A = 0$$

$$-KT \ln \underbrace{\frac{\frac{2\pi m_C KT}{h^2}\frac{A}{M}}{\frac{2\pi m_A KT}{h^2}\frac{A}{M}\;\frac{2\pi m_B KT}{h^2}\frac{A}{M}}}_{X} - KT \ln \underbrace{\frac{q_{rot_C}\, q_{vib_C}^{0}}{q_{rot_B}\, q_{vib_B}^{0}\; q_{rot_A}\, q_{vib_A}^{0}}}_{Y} + E_{bind}$$

$$+ E_{bind,C} + ZPE_C - E_{bnd,A} + ZPE_A - E_{bnd,B} - ZPE_B$$

$$+ KT \ln \frac{\theta_C}{\theta_B \cdot \theta_A} = 0.$$

$K(1 + \ln S_T)$

$$-KT \ln XY + \underbrace{\Delta E_{rxn}}_{DFT} = -KT \ln \frac{\theta_C}{\theta_B \theta_A}$$

$$\boxed{K = \exp\left(\frac{-\Delta G^0}{KT}\right)}$$

$$-\left(\frac{-KT \ln XY + \Delta E_{rxn}}{KT}\right) = \ln \frac{\theta_C}{\theta_B \theta_A}.$$

$$K = \frac{\theta_C}{\theta_B \theta_A}$$

$$\exp\left(-\left(\frac{-KT \ln XY + \Delta E_{rxn}}{KT}\right)\right) = K.$$

$$\Delta G^0 = \Delta E_{rxn} + KT \ln XY.$$

$$= \Delta H^0 - T\,\Delta S^0$$

$$K = \exp\left(-\Delta G^0 / KT\right)$$