Physics 201 Day 27

Quiz 4.0 Wednesday: Ideal Gas Law

$$PV = N k_B T$$

$$G = E - TS \qquad \beta = \frac{1}{k_B T}$$

$$P_1 = \frac{e^{-G_1 \beta}}{Z} \qquad S = k_B \ln \Omega$$

$$Z = \sum_{\text{all } i} e^{-\beta G_i}$$

Examples: 2 states (will put in numbers)

$$Z = e^{-\beta G_1} + e^{-\beta G_2}$$

$$P_1 = \frac{e^{-\beta G_1}}{e^{-\beta G_1} + e^{-\beta G_2}} \cdot \frac{e^{\beta G_1}}{e^{\beta G_1}} = \frac{1}{1 + e^{-\beta \Delta G}}$$

$$\Delta G = G_2 - G_1$$

$P_2 = 1 - P_1$ Duh.

$$P_1 = \frac{1}{1 + e^{\beta \Delta G}}$$

$$\Delta G = G_2 - G_1 = E_2 - TS_2 - (E_1 - TS_1)$$

$$= E_2 - E_1 - T(S_2 - S_1)$$

$$\Delta G = \Delta E - T\Delta S$$

Ex1 state 1: $E_1 = 0$ $S_1 = 0$

state 2: $E_2 = +1 \frac{\text{kcal}}{\text{mol}}$ $S_2 = 0.005 \frac{\text{kcal}}{\text{mol} \cdot \text{K}}$

Find P of each at: $T = 100\text{K}$, 300K, 600K.

$$P_1 = \frac{1}{1 + e^{-\Delta G \beta}}$$

$$\beta = \frac{1}{k_B T}$$

$$k_B = 0.002 \frac{\text{kcal}}{\text{mol} \cdot \text{K}}$$

ΔG at 100K: $1 \frac{\text{kcal}}{\text{mol}} - 0 - 100\text{K}(0.005 - 0)$ $\frac{\text{kcal}}{\text{mol} \cdot \text{K}}$

$= (1 - 0.5) \frac{\text{kcal}}{\text{mol}}$

$= 0.5 \frac{\text{kcal}}{\text{mol}}$

$$\beta = \frac{1}{0.002 \times 100} = \frac{1}{0.2} = 5 \frac{\text{mol}}{\text{kcal}}$$

$$e^{-\beta \Delta G} = e^{-5 \cdot \frac{1}{2}} = 0.0821$$

$P_1 = 0.924$

$P_2 = 0.076$ at 100K.

at 600K: $\quad \Delta E \quad - T\,\Delta S \quad \frac{\text{kcal}}{\text{mol}\cdot\text{K}}$

$$\Delta G = 1\,\frac{\text{kcal}}{\text{mol}} - 0 - 600\text{K}\,(0.005 - 0)$$

$$= (1 - 3)\,\frac{\text{kcal}}{\text{mol}} = -2\,\frac{\text{kcal}}{\text{mol}}$$

$$\beta = \frac{1}{0.002 \times 600} = \frac{1}{1.2} = 0.833\,\frac{\text{mol}}{\text{kcal}}$$

$$e^{-\beta\Delta G} = e^{-0.833(-2)} = e^{1.\overline{6}} = 5.29$$

$$P_1 = \frac{1}{1+e^{-\beta\Delta G}} = \frac{1}{1+5.29} = \frac{1}{6.29} = 0.159$$

$$P_2 = 1 - P_1 = 0.841$$

At what T is $P_1 = P_2$? Call that T^*

$$P_1 = \frac{1}{1+e^{-\beta\Delta G}} \quad \text{at } T^*,\ P_1 = \frac{1}{2} = \frac{1}{1+e^{-\beta\Delta G}}$$

$$e^{-\beta\Delta G} = 1 \quad \text{take ln of each side}$$

$$-\beta\Delta G = \ln(1) = 0$$

$$-\frac{\Delta G}{k_B T^*} = 0 \quad \text{Thus } \Delta G = 0 \text{ at } T^*$$

$$\Delta G = \Delta E - T\Delta S$$

$$\Delta E = T^* \Delta S$$

$$\frac{\Delta E}{\Delta S} = T^* = \frac{1\,\frac{\text{kcal}}{\text{mol}}}{0.005\,\frac{\text{kcal}}{\text{mol}\cdot\text{K}}} = 200\text{ K}$$

<u>If</u> $T^* < 0$, No real T when $P_1 = P_2$ thus <u>one</u> state is al<u>w</u>ays more favorable.

<u>Ex:</u> The Disfavored State:

State ① $E_1 = 0$ $S_1 = 0$

State ② $E_2 = 1\,\frac{\text{kcal}}{\text{mol}}$ $S_2 = -0.005\,\frac{\text{kcal}}{\text{mol}\cdot\text{K}}$

$$P_1 = \frac{1}{1 + e^{-\beta\Delta G}}$$

$$\Delta G = E_2 - E_1 - T(S_2 - S_1)$$

$$= 1\,\frac{\text{kcal}}{\text{mol}} - T\left(-0.005\,\frac{\text{kcal}}{\text{mol}\cdot\text{K}}\right)$$

At low T,

$$P_1 = \frac{1}{1+e^{-\frac{\Delta G}{k_B T}}}$$ ← look at this.

$$\frac{\Delta G}{k_B T} = \frac{\Delta E - T\Delta S}{k_B T} = \frac{\Delta E}{k_B T} - \frac{\Delta S}{k_B}$$

as $T \to \infty$...

$$P_1 = \frac{1}{1+e^{\Delta S/k_B}} = \frac{1}{1+e^{-5/2}}$$

$= \cancel{0.0821}$ 0.924 (not zero... always some in S_1).

$$P_2 = 1 - P_1 = \cancel{0.918}\ 0.076$$

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as $T \to 0$...

$$\frac{\Delta G}{k_B T} = \frac{\Delta E}{k_B T} - \frac{\Delta S}{k_B} \approx \frac{\Delta E}{k_B T}$$

$$P_1 = \frac{1}{1+e^{-\Delta E/k_B T}} \to 1 \quad \cancel{\to 0} \times \frac{e^{\Delta E/k_B T}}{e^{\Delta E/k_B T}}$$

$$P_2 = 0$$

e^{-x} for large x

$$e^{-x} \simeq 1 - x + \frac{x^2}{2} - \cdots$$

$$P_1 = \frac{e^{\Delta E/k_B T}}{\underbrace{e^{\Delta E/k_B T}}_{\text{enormous}} + \underbrace{1}_{\text{throw out}}} \rightarrow 1$$

If $T^* = 300K$, and $E_2 = 2\frac{kcal}{mol}$ more than E_1, find $\Delta S = S_2 - S_1$.

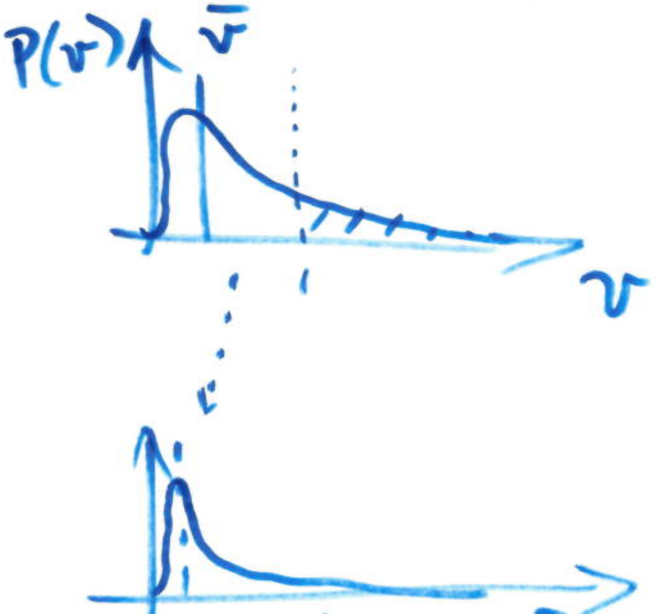
$\Delta E = 2\frac{kcal}{mol}$

$$T^* = \frac{\Delta E}{\Delta S} = \frac{2\frac{kcal}{mol}}{\Delta S} = 300K$$

$$\Delta S = \frac{2\frac{kcal}{mol}}{300K} = 6.67 \times 10^{-3} \frac{kcal}{mol \cdot K}$$

Note: ΔS often expressed as $\frac{cal}{mol \cdot K}$ for this reason.

$$\Delta S = 6.67 \frac{cal}{mol \cdot K}$$



new, lower $\bar{v}$

If T = 330K, $P_1 = 3P_2$

and E_1 = 4 kcal/mol lower than E_2

find ΔS.

$$P_1 + P_2 = 1$$

$$3P_2 + P_2 = 1 \rightarrow P_2 = \frac{1}{4} \quad P_1 = \frac{3}{4}$$

$$\left.\frac{P_1}{P_2} = 3 = \frac{e^{-G_1 B}}{e^{-G_2 B}}\right\}$$

trick... you can try.

$$P_1 = \frac{1}{1 + e^{-\Delta G B}} = \frac{3}{4}$$

find ΔG then find ΔS.