Department of Chemical Engineering
University of California, Santa Barbara

ChE 170
Fall 2010

Handout 2: Molecular Thermodynamics

Boltzmann Law

Consider all possible molecular *configurations* of a system. Let a particular configuration be denoted by the index m. At some temperature T, Boltzmann's law states that the fraction of the time the system will spend in that configuration is given by

$$\wp_m = C e^{\frac{-U_m}{k_B T}}$$

where U_m is the energy of the configuration and C is a constant. These probabilities must sum to unity when one considers all possible configurations of a system. Thus, we must have

$$\sum_m \wp_m = 1$$

Plugging in the expression above,

$$\sum_m C e^{\frac{-U_m}{k_B T}} = 1 \quad \rightarrow \quad C \sum_m e^{\frac{-U_m}{k_B T}} = 1 \quad \rightarrow \quad C = \left(\sum_m e^{\frac{-U_m}{k_B T}} \right)^{-1}$$

Therefore, a general expression for the probability, without the constant, is

$$\wp_m = \frac{e^{\frac{-U_m}{k_B T}}}{\sum_{m'} e^{\frac{-U_{m'}}{k_B T}}}$$

Configurations versus states

Oftentimes we are interested not in specific configurations, but rather, more general *states* that could involve a collection of different configurations. Some examples of different states:

bound versus unbound

folded versus unfolded

phosphorylated versus unphosphorylated

To find the fraction of the time that a system spends in a specific state, we need to sum up the fraction of the time that it spends in all configurations that belong to that state:

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Now we consider a simplification. We will assume that all of the configurations in a state have the same energy $U_m = U_{\text{state}}$. That means that each term in the sum above will have the same

value. We will denote the number of configurations in the state by $\Omega(\text{state})$. Then, we can write,

$$\wp(\text{state}) = C\Omega(\text{state})e^{\frac{-U_{\text{state}}}{k_B T}}$$

But we recognize that $S(\text{state}) = k_B \ln \Omega(\text{state})$ and so we can write,

$$\begin{aligned}\wp(\text{state}) &= Ce^{\frac{TS}{k_B T} - \frac{U_{\text{state}}}{k_B T}} \\ &= Ce^{-\frac{A_{\text{state}}}{k_B T}}\end{aligned}$$

where we have identified $A_{\text{state}} = U_{\text{state}} - TS_{\text{state}}$. If the system is at constant pressure, this expression takes on a slightly different form (which we present here without derivation):

$$\wp(\text{state}) = Ce^{-\frac{G_{\text{state}}}{k_B T}}$$

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Fall 2010

Handout 2: Molecular Thermodynamics

Boltzmann Law

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Handout 2: Molecular Thermodynamics

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$$\sum_m C e^{\frac{-U_m}{k_B T}} = 1 \quad \rightarrow \quad C \sum_m e^{\frac{-U_m}{k_B T}} = 1 \quad \rightarrow \quad C = \left(\sum_m e^{\frac{-U_m}{k_B T}} \right)^{-1}$$

Therefore, a general expression for the probability, without the constant, is

$$\wp_m = \frac{e^{\frac{-U_m}{k_B T}}}{\sum_{m'} e^{\frac{-U_{m'}}{k_B T}}}$$

Configurations versus states

Oftentimes we are interested not in specific configurations, but rather, more general *states* that could involve a collection of different configurations. Some examples of different states:

bound versus unbound

folded versus unfolded

phosphorylated versus unphosphorylated

To find the fraction of the time that a system spends in a specific state, we need to sum up the fraction of the time that it spends in all configurations that belong to that state:

$$\begin{aligned} \wp(\text{state}) &= \sum_{m \in \{\text{state}\}} \wp_m \\ &= C \sum_{m \in \{\text{state}\}} e^{\frac{-U_m}{k_B T}} \end{aligned}$$

Now we consider a simplification. We will assume that all of the configurations in a state have the same energy $U_m = U_{\text{state}}$. That means that each term in the sum above will have the same

value. We will denote the number of configurations in the state by $\Omega(\text{state})$. Then, we can write,

$$\wp(\text{state}) = C\Omega(\text{state})e^{\frac{-U_{\text{state}}}{k_B T}}$$

But we recognize that $S(\text{state}) = k_B \ln \Omega(\text{state})$ and so we can write,

$$\begin{aligned}\wp(\text{state}) &= Ce^{\frac{TS}{k_B T} - \frac{U_{\text{state}}}{k_B T}} \\ &= Ce^{-\frac{A_{\text{state}}}{k_B T}}\end{aligned}$$

where we have identified $A_{\text{state}} = U_{\text{state}} - TS_{\text{state}}$. If the system is at constant pressure, this expression takes on a slightly different form (which we present here without derivation):

$$\wp(\text{state}) = Ce^{-\frac{G_{\text{state}}}{k_B T}}$$

where G_{state} gives the Gibbs free energy of that state. Now, to find the constant of normalization, we take a similar approach as before. We consider that the sum of probabilities over all possible states must equal unity,

$$\sum_{\text{states } i} \wp(i) = 1 \quad \rightarrow \quad C \sum_{\text{states } i} e^{-\frac{G_i}{k_B T}} = 1 \quad \rightarrow \quad C = \left(\sum_{\text{states } i} e^{-\frac{G_i}{k_B T}} \right)^{-1}$$

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Handout 2: Molecular Thermodynamics

Boltzmann Law

Consider all possible molecular *configurations* of a system. Let a particular configuration be denoted by the index m. At some temperature T, Boltzmann's law states that the fraction of the time the system will spend in that configuration is given by

$$\wp_m = Ce^{\frac{-U_m}{k_B T}}$$

where U_m is the energy of the configuration and C is a constant. These probabilities must sum to unity when one considers all possible configurations of a system. Thus, we must have

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Plugging in the expression above,

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ChE 170
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