LS2103: MIDSEM Answer Key

Solution 1

   i b   **Marks: 2**

   ii d   **Marks: 2**

   iii e   **Marks: 2**

Solution 2(i)

Since the gas given is an ideal gas, the term E has no component provided by the intermolecular forces.
The system is closed and therefore Energy is constant. **Marks: 1**
E is directly proportional to Temperature. **Marks: 1**

Solution 2(ii)

Given: Volume increases from V to $1.5V$

For initial condition:

$$S_1 = K_B \ln \left[(2mE)^{3/2} V \right]^N + B$$

For final condition:

$$S_2 = K_B \ln \left[(2mE)^{3/2} (1.5V) \right]^N + B$$

Change in entropy:

$$\Delta S = S_2 - S_1$$

Marks: 1

$$= K_B \ln \left[\frac{(2mE)^{3/2}(1.5V)}{(2mE)^{3/2}V} \right]^N + B - B$$

$$= K_B N \ln \left[\frac{(2mE)^{3/2}(1.5V)}{(2mE)^{3/2}V} \right]$$

$$= N K_B \ln(1.5)$$

$$= N K_B (0.405) \text{ Joule/Kelvin}$$

Marks: 1

Since, $\Delta S > 0$, the expansion is spontaneous. **Marks: 1**

Solution 2(iii)

Given: $N = N_A$ **Marks: 1**

$$S_2 - S_1 = 0.405 N K_B = 0.405 N_A K_B$$

$$= 0.405 \cdot 6.022 \times 10^{23} \cdot 1.381 \times 10^{-23}$$

$$= 3.371 \text{ Joule/Kelvin}$$

Marks: 2

For people who took V in the denominator:

Solution 2(ii)

$$S_2 - S_1 = N K_B \ln\left(\frac{V}{1.5V}\right)$$

Marks: 0.5

$$= -0.405 N K_B \text{ Joule/Kelvin}$$

Marks: 1

Since, $S_2 - S_1 < 0$, the expansion is non-spontaneous.   **Marks: 0.5**

Solution 2(iii)

Given: $N = N_A$ **Marks: 1**

$$S_2 - S_1 = -3.371 \text{ Joule/Kelvin}$$

Marks: 1

Solution 3(i)

We are given a small peptide molecule in solution with M number of possible energy states, with the j-th state having probability P_j. Using Shannon's formula, the level of disorder (entropy) in the system is given by:

$$I = -NK \sum_{j=1}^{M} P_j \ln(P_j)$$

where:
N is the number of states/configurations the peptide can be in
$K = \frac{1}{\ln(2)}$ **Marks: 2**

Solution 3(ii)

We know that

$$\sum_{j=1}^{M} P_j = 1 \Rightarrow P_1 = 1 - \sum_{j=2}^{M} P_j$$

.

Therefore, the disorder can be written as: **Marks: 1**

$$I = -NK\left[P_1\ln(P_1) + \sum_{j=2}^{M} P_j\ln(P_j)\right] = -NK\left[(1 - \sum_{j=2}^{M} P_j)\ln(1 - \sum_{j=2}^{M} P_j) + \sum_{j=2}^{M} P_j\ln(P_j)\right]$$

For maximum disorder, $\frac{\partial I}{\partial P_i} = 0$ for some i. Using $\frac{\partial}{\partial x}(x\ln(x)) = \ln(x) + 1$, and the fact that the events are mutually independent, we have $\frac{\partial}{\partial P_i}\left(\sum_{j=2}^{M} P_j\ln(P_j)\right) = \ln(P_i) + 1$. Using these: **Marks: 1**

$$\frac{\partial I}{\partial P_i} = (-NK)\left[\frac{\partial}{\partial P_i}\left((1 - \sum_{j=2}^{M} P_j)\ln(1 - \sum_{j=2}^{M} P_j)\right) + \ln(P_i) + 1\right] = 0$$

$$\Rightarrow (1 - \sum_{j=2}^{M} P_j) * \frac{\partial}{\partial P_i}\left(\ln(1 - \sum_{j=2}^{M} P_j)\right) + \ln(1 - \sum_{j=2}^{M} P_j) * \frac{\partial}{\partial P_i}\left(1 - \sum_{j=2}^{M} P_j\right) + \ln(P_i) + 1 = 0$$

$$\Rightarrow (1 - \sum_{j=2}^{M} P_j) \cdot \frac{1}{(1 - \sum_{j=2}^{M} P_j)} \cdot \frac{\partial}{\partial P_i}\left(1 - \sum_{j=2}^{M} P_j\right) - \ln(1 - \sum_{j=2}^{M} P_j) + \ln(P_i) + 1 = 0$$

$$\Rightarrow -1 - \ln(1 - \sum_{j=2}^{M} P_j) + \ln(P_i) + 1 = 0$$

$$\Rightarrow \ln\left(\frac{P_i}{1 - \sum_{j=2}^{M} P_j}\right) = 0$$

$$\Rightarrow P_i = 1 - \sum_{j=2}^{M} P_j = P_1 \quad \text{for any } i = 1, 2, ..., n$$

Marks: 1

Therefore, for all peptides, the maximum disorder occurs when all states have the same probability.

The level of disorder is minimum when the protein can be found in just one energy state with absolute certainty. That is, for some i:

$$P_i = 1 \quad \text{and} \quad P_j = 0 \quad \forall j \neq i$$

In that case, the disorder becomes: **Marks: 1**

$$I = -NK\sum_{j=1}^{M} P_j\ln(P_j) = -NK\left[P_i\ln(P_i) + \sum_{j=1, j\neq i}^{M} P_j\ln(P_j)\right]$$

$$= -NK\left[1 \cdot \ln(1) + \sum_{j=1, j\neq i}^{M} 0 \cdot \ln(P_j)\right] = 0$$

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Therefore, the disorder will be zero.

Solution 3(iii)

The probability of occupation of the i-th state with energy E_i is:

$$P_i \propto e^{-\beta E_i} \Rightarrow P_i = P_0 e^{-\beta E_i} \quad \text{(Boltzmann distribution)}$$

where P_0 is the proportionality constant, $\beta = \frac{1}{k_B T}$, k_B is the Boltzmann constant, and T is the absolute temperature. **Marks: 1**

Substituting this in Shannon's formula, we get:

$$
\begin{aligned}
I &= -NK \sum_{j=1}^{n} P_j \ln(P_j) = -NK \sum_{j=1}^{n} P_0 e^{-\beta E_j} \ln(P_0 e^{-\beta E_j}) \\
&= -NK \sum_{j=1}^{n} P_0 e^{-\beta E_j} \left[\ln(P_0) + \ln(e^{-\beta E_j}) \right] \\
&= -NK \sum_{j=1}^{n} P_0 e^{-\beta E_j} \left[\ln(P_0) - \beta E_j \right] \\
&= -NK \left[P_0 \ln(P_0) \sum_{j=1}^{n} e^{-\beta E_j} - P_0 \beta \sum_{j=1}^{n} E_j e^{-\beta E_j} \right]
\end{aligned}
$$

Since $\sum_{j=1}^{n} e^{-\beta E_j} = \frac{1}{P_0} = Z$ (partition function) and $\sum_{j=1}^{n} E_j e^{-\beta E_j} = \langle E \rangle$, the average internal energy, we have: **Marks: 1**

$$
\begin{aligned}
\frac{-I}{NK} &= P_0 \ln(P_0) \frac{1}{P_0} - P_0 \beta \langle E \rangle \\
&= \ln\left(\frac{1}{Z}\right) - \frac{\beta \langle E \rangle}{Z}
\end{aligned}
$$

Solution 4(i)

Most probable configuration: D **Marks: 1**

Reason:
The population of each energy state is given by:

$$P_i \propto e^{(-\beta E_i)}$$

Marks: 1

Now the free energy for D is the least; hence for the least E_i, the P_i will be maximum. Thus, D is the most favorable state. It has the least energy and therefore the most stable.

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Equations:

$$E_I = -9 \, \text{kcal/mol}$$
$$E_D = -11 \, \text{kcal/mol}$$
$$E_N = -10.5 \, \text{kcal/mol}$$
$$\frac{P_D}{P_I} = e^{(\beta(E_I - E_D))} = e^{(2\beta)}$$
$$\frac{P_D}{P_N} = e^{(\beta(E_N - E_D))} = e^{(0.5\beta)}$$

<div align="right">**Marks: 1**</div>

Now,

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

where $k_B T = 0.6 \, \text{kcal/mol}$ at $300 \, \text{K}$.

$$\frac{P_D}{P_I} = e^{(2 \cdot 1.67)} = 28.22$$
$$\frac{P_D}{P_N} = e^{(0.5 \cdot 1.67)} = 2.30$$

<div align="right">**Marks: 1**</div>

Solution 4(ii)

Energy Values:

$$E_{TS1} = -5.5 \, \text{kcal/mol}$$
$$E_{TS2} = -6.5 \, \text{kcal/mol}$$
$$E_I = -9 \, \text{kcal/mol}$$

For $I \to N$:

$$\text{Energy barrier} = E_{TS2} - E_I$$
$$= -6.5 - (-9)$$
$$= 2.5 \, \text{kcal/mol}$$

<div align="right">**Marks: 1**</div>

For $I \to D$:

$$\text{Energy barrier} = E_{TS1} - E_I$$
$$= -5.5 - (-9)$$
$$= 3.5 \, \text{kcal/mol}$$

<div align="right">**Marks: 1**</div>

From the Arrhenius rate law:

$$\text{rate} \propto e^{-\beta(\text{energy barrier})}$$ **Marks: 1**

$$\frac{r_{I \to N}}{r_{I \to D}} = \frac{e^{-\beta(2.5)}}{e^{-\beta(3.5)}}$$

$$= e^{\beta}$$

$$= e^{1.67}$$

$$= 5.3$$

Marks: 1