Name: Date:

# Partial Exam

**Biophysics**
*Bioinformatics degree*

**1)** (1 point) We have a methane ($CH_4$) gas in a container. A sensor determines that the average kinetic energy of methane molecules is 6.4 x $10^{-21}$ J. Determine the temperature and the most probable velocity of the gas molecules in this container.

To obtain the temperature we could use the following expressions:

$$\langle K_E \rangle = \frac{1}{2} m (v^{rms})^2 \qquad v^{rms} = \sqrt{(3RT/M)} = \sqrt{(3k_B T/m)}$$

we obtain:

$$T = \frac{2}{3k_b} K_E = 309\,K$$

To obtain the most probable velocity, M has to be in kg/mol:

$$v^{mp} = \sqrt{(2RT/M)} = 567\,m/s$$

**2)** (1.5 points) We have a system of 3 levels at 20ºC with the corresponding energies ($e_0$=1 kJ/mol, $e_1$=2 kJ/mol and $e_2$=3 kJ/mol).

a) Calculate the energy of the following configurations: {9, 6, 1}, {10, 4, 2}, {11, 2, 3} and {12, 0, 4}.

b) Calculate the *weight* and the entropy of the previous configurations. Discuss which configuration is the most probable.

a) $E = e_0 * n_0 + e_1 * n_1 + e_2 * n2$

$$E_{\{9,6,1\}} = E_{\{10,4,2\}} = E_{\{11,2,3\}} = E_{\{12,0,4\}} = 24\,kJ/mol$$

b)

$$W = \frac{N!}{n_0! n_1! n_2!} \qquad S = k_b \ln(W)$$

$$W_{\{9,6,1\}} = \frac{16!}{9!6!1!} = 80080 \qquad W_{\{10,4,2\}} = 120120 \qquad W_{\{11,2,3\}} = 43680 \qquad W_{\{12,0,4\}} = 1820$$

$$S_{\{9,6,1\}} = 1.56 \cdot 10^{-22}\,J/K \qquad S_{\{10,4,2\}} = 1.61 \cdot 10^{-22}\,J/K \qquad S_{\{11,2,3\}} = 1.48 \cdot 10^{-22}\,J/K$$

$S_{\{12,0,4\}}=1.04\cdot 10^{-22}\,J/K$

It is also correct to use $S=R\ln(W)$ and to give the values of entropy in term of *J/(K·mol)*
The most probable configuration is the one with the highest weight: {10,4,2}.

**3)** (1.5 points) Consider a three-level system with energy levels: 0, 2 kJ/mol and 3 kJ/mol. Calculate the population corresponding to these energy levels at T=60ºC. Comment what happens with the population of highest level (3 kJ/mol) if the temperature is increased. And what happens with this level (3 kJ/mol) if the most stable level (0 kJ/mol) were degenerated with multiplicity of 2.

$$q=\sum_{i=1}^{3} e^{-\beta e_i}=1.82 \qquad \beta=\frac{1}{k_b T}\text{ or }\frac{1}{RT}$$

$$p_0=\frac{e^{-\beta e_i}}{q}=0.55 \qquad p_1=\frac{e^{-\beta e_1}}{q}=0.27 \qquad p_2=\frac{e^{-\beta e_2}}{q}=0.18$$

If the temperature is increased, the population of the highest energetic level increases. In the limit of high temperature, the three states will have a population of 1/3.
If the most stable level is degenerated with multiplicity of 2, the population of the highest energetic level decreases. In the limit of high temperature, the four states will have a population of 1/4.

**4)** (1 point) Starting from the differential form of the reaction rate of a second order reaction $-d[A]/dt=k[A]^2$ obtain the expression for the integrated form of the velocity and the expression for the half live.

$$\int -d[A]/dt=\int k[A]^2 \qquad \int_{A_0}^{A_t} -d[A]/[A]^2=\int_0^t k\,dt \qquad \frac{1}{A}=\frac{1}{A_0}+kt$$

To obtain the expression for the half live, $A=A_0/2$

$$\frac{1}{A_0/2}=\frac{1}{A_0}+k t_{1/2} \qquad t_{1/2}=\frac{1}{A_0 k}$$

**5)** (1 point) a) In the collision theory, it is supposed that an activated complex is in equilibrium with the reactants. Indicate if this sentence is true or false. If it is false indicate why.
FALSE. The activated complex is defined in the TST (Transition State Theory) not in the Collision Theory.
b) The Boltzmann distribution gives the numbers of molecules in each state of a system at any temperature. Indicate if this sentence is true or false. If it is false indicate why.
TRUE.

**6)** (1 point) The half-live of pyruvic acid in the presence of an aminotransferase enzyme (which converts it to alanine) was found to be 221 s. How long will it take for the concentration of pyruvic acid to fall to 1/64 of its initial value in this first-order reaction?

$$k=\frac{\ln 2}{t_{1/2}}=3.1\cdot 10^{-3}s^{-1}$$

$$A_0/64=A_0*e^{-kt_{1/64}} \qquad t_{1/64}=1326s$$

**7)** (1.5 point) The following kinetic data ($v_0$ is the initial rate) were obtained for the reaction 2 ICl(g) + $H_2$ → $I_2$ (g) + 2 HCl(g):

| **Experiment** | **$[ICl]_0$/ (mmol dm$^{-3}$)** | **$[H_2]_0$/ (mmol dm$^{-3}$)** | **$v_0$/ (mol dm$^{-3}$ s$^{-1}$)** |
|---|---|---|---|
| 1 | 1.5 | 1.5 | 3.7 x $10^{-7}$ |
| 2 | 3.0 | 1.5 | 7.4 x $10^{-7}$ |
| 3 | 3.0 | 4.5 | 22 x $10^{-7}$ |
| 4 | 4.7 | 2.7 | ? |

a) Write the rate law for the reaction.

$$v_1=k[\mathrm{ICl}]_1^{\alpha}[\mathrm{H\_2}]_1^{\beta}$$
$$v_2=k[\mathrm{ICl}]_2^{\alpha}[\mathrm{H\_2}]_2^{\beta}$$
$$v_3=k[\mathrm{ICl}]_3^{\alpha}[\mathrm{H\_2}]_3^{\beta}$$
$$v_4=k[\mathrm{ICl}]_4^{\alpha}[\mathrm{H\_2}]_4^{\beta}$$

$$\alpha=\frac{\ln\frac{v_1}{v_2}}{\ln\frac{[\mathrm{ICl}]_1}{[\mathrm{ICl}]_2}} \qquad \beta=\frac{\ln\frac{v_2}{v_3}}{\ln\frac{[\mathrm{ICl}]_2}{[\mathrm{ICl}]_3}}\simeq 1$$

`Rate law:` $v=k[\mathrm{ICl}][\mathrm{H\_2}]$

b) Determine the value of the rate constant.

$$k = \frac{v_1}{[ICl]_1 [H\_2]_1} = 0.16 \frac{dm^3}{mol \cdot s}$$

c) Use the data to predict the reaction rate for experiment 4.

$$v_4 = k [ICl]_4 [H\_2]_4 = 2.1 \cdot 10^{-6} \frac{mol}{dm^3 \cdot s}$$

**8)** (1.5 point) The Arrhenius parameters for the reaction of decomposition of cyclobutane $C_4H_8(g) \rightarrow 2\ C_2H_4(g)$ are $\log(A/s^{-1})=15.6$ and $E_a= 261$ kJ mol$^{-1}$. What is the half-live of this first-order reaction at 20ºC and 500ºC?

$$k = A e^{\frac{-Ea}{RT}}$$

$$k_{20°C} = 1.2 \cdot 10^{-31} s^{-1} \qquad t_{1/2} = \frac{\ln 2}{k_{20°C}} = 6.2 \cdot 10^{30} s$$

$$k_{500°C} = 9.0 \cdot 10^{-3} s^{-1} \qquad t_{1/2} = \frac{\ln 2}{k_{500°C}} = 77 s$$

**Additional data:**

M(H)=1 g mol$^{-1}$; M(C)=12 g mol$^{-1}$; M(O)=16 g mol$^{-1}$; M(N)=14 g mol$^{-1}$
$k_B$=1.3806488·10$^{-23}$ J K$^{-1}$
R=8.314 J K$^{-1}$ mol$^{-1}$
R=0.082 atm L K$^{-1}$ mol$^{-1}$
$N_A$=6.022·10$^{23}$ mol$^{-1}$

$$v^{mp} = \sqrt{(2RT/M)}$$

$$\bar{v} = \sqrt{(8RT/(\pi M))}$$

$$v^{rms} = \sqrt{(3RT/M)}$$

$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv/(2k_B T)}$$

$$\frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0 [A]}{[A]_0 [B]} = kt$$