

IMPERIAL COLLEGE LONDON

B.Eng., M.Eng and ACGI Examinations 2018
Part 1

Biomedical Engineering

BE1-HTDK Thermodynamics and Kinetics

Wednesday 24 May 2018, 14:00-15:30pm

Duration: 1.5 hour

The paper has **FOUR** questions.

Answer **ALL FOUR** questions.

Marks for questions and parts of questions are shown next to the question. The marks for questions (and parts thereof) are indicative, and they may be slightly moderated at the discretion of the Examiner

Quadratic formula $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Gas constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$0^\circ\text{C} = 273.15 \text{ K}$

Boltzmann's constant $k_B = 1.380658 \times 10^{-23} \text{ J K}^{-1}$

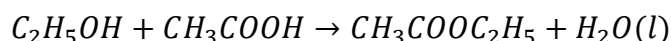
Avagadro's number, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

The permittivity of free space is $8.85 \times 10^{-12} \text{ F m}^{-1}$

The Stefan-Boltzmann constant $5.67 \times 10^{-8} \text{ W/m}^2\text{K}^4$

The charge on an electron is $1.60 \times 10^{-19} \text{ C}$ or $9.647 \times 10^4 \text{ C mol}^{-1}$.

- 1 a) State the first two laws of thermodynamics. **10 marks**
- b) Define the following systems: open, closed, isolated, adiabatic, diathermic. **10 marks**
- c) Derive an expression for the work done by the system for the isothermal reversible expansion of an ideal gas. **20 marks**
- d) Define constant pressure heat capacity, C_p and derive an expression showing how enthalpy varies with pressure. Clearly state all assumptions. **20 marks**
- e) Ethanol (C_2H_5OH) can react with acetic acid (CH_3COOH) to form ethyl acetate ($CH_3COOC_2H_5$). The balanced reaction is:



Some thermodynamic data for the chemical species involved are given below:

Compound	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$C_p / \text{J mol}^{-1} \text{K}^{-1}$
$H_2O(l)$	-285.83	75.291
C_2H_5OH	-277.69	111.46
CH_3COOH	-484.5	124.3
$CH_3COOC_2H_5$	-479.0	170.1

ΔH_f° is the enthalpy of reaction at 298.15 K, 1 standard atmosphere. C_p is the constant pressure heat capacity at 298.15 K

- (i) Calculate the enthalpy of reaction **15 marks**
- (ii) Calculate the change in C_p the constant pressure heat capacity for the reaction. **15 marks**
- (iii) Calculate the enthalpy of reaction at 750 K and clearly state all assumptions. **10 marks**

Question total =100 marks

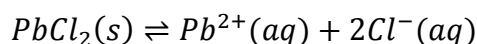
- 2 a) List the principal intermolecular forces in aqueous solution and give their typical energies.

20 marks

b) What is the Bjerrum Length? Derive an expression for this variable and calculate its value in pure water at 298.15 K. The relative permittivity of water is 78.54. The permittivity of free space is 8.85×10^{-12} . The charge on an electron is 1.6×10^{-19} C. Boltzmann's constant is 1.380658×10^{-23} J K⁻¹.

20 marks

c) A saturated solution of lead (II) chloride, PbCl₂ was prepared at 298.15 K. The dissolution can be represented as:



On analysis, the concentration of Pb²⁺ was found to be 15.9 mmol dm⁻³. Show that this is consistent with the solubility product for PbCl₂ being 1.6×10^{-5} .

15 marks

d) Calculate the solubility of lead chloride in water where the initial concentration of Pb²⁺ was 1 mmol dm⁻³.

20 marks

e) Define pH acid dissociation constant K_a and pK_a and rank the following acids in order of increasing acid strength:

Substance	pK_a
Acetic acid	4.76
Ascorbic acid	4.17
Phenol	9.95
Benzoic acid	4.20
Hydrogen cyanide	9.21

Which, if any, of these compounds will be in the protonated (un-ionised) forms in pH 7.4 buffer solution. Justify your answer.

25 marks

Question total = 100 marks

3 a) What are the important properties of a state function?

15 marks

b) Is the following equation a state function? Explain your answer

$$dT = \frac{p}{R} dV + \frac{V}{R} dp$$

10 marks

c) Given:

$$U = H - pV$$
$$G = H - TS$$

the first law of thermodynamics and the Clausius relationship:

$$dS = \frac{\delta q_{rev}}{T}$$

(i) Show that:

$$dG = Vdp - SdT$$

Clearly state all assumptions.

25 marks

(ii) Derive the Gibbs-Helmholtz equation:

$$\left(\frac{\partial \left(\frac{G}{T} \right)}{\partial T} \right)_p = -\frac{H}{T^2}$$

showing the temperature dependence of free energy.

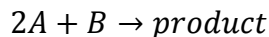
40 marks

(iii) Show how Gibbs free energy varies with pressure.

10 marks

Question total = 100 marks

- 4 a) For the third order reaction:



Where B is present in large excess so that its concentration does not change significantly during the course of the reaction, show that the integrated rate law is given by:

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + k[B]_0 t$$

20 marks

- b) Derive an expression for the half-life of the reaction in (a).

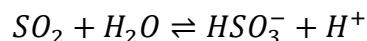
10 marks

c) Sulfur dioxide, SO_2 is widely used as a preservative and is an important component of acid rain. Its Henry's Law constant in water at 298.15 K is $1.18 \times 10^{-5} \text{ mol dm}^{-3} \text{ Pa}^{-1}$. The median partial pressure of SO_2 in Beijing is $1.16 \times 10^{-3} \text{ Pa}$.

- (i) Calculate the aqueous concentration of sulfur dioxide in rainwater in Beijing.

10 marks

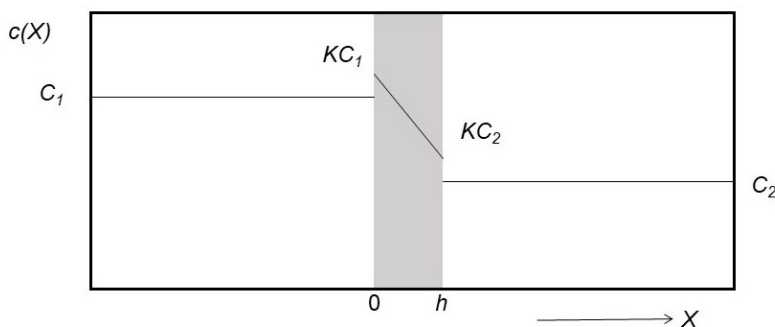
- (ii) Sulfur dioxide reacts in water according to the reaction below:



The pK_a of this reaction is 1.81. Predict the pH of the rainwater. Make all your assumptions clear.

15 marks

d) Two large volume well-stirred solutions of glucose are separated by a permeable membrane of thickness h such that the concentrations in the solution remain homogeneous. The concentrations of glucose in the two compartments are c_1 and c_2 where $c_1 > c_2$. This is shown schematically below, with the membrane shaded in grey:



Question 4 continues overleaf

The partition constant for glucose dissolving in the membrane is given by:

$$K = \frac{c_{mem}}{c_{sol}}$$

Where c_{mem} is the concentration of the glucose in the membrane and c_{sol} is the concentration in solution (i.e. c_1 on one side and c_2 on the other side). The diffusion coefficient for glucose in the membrane is given by D . Fick's second law of diffusion in one dimension is:

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2}$$

Solve this equation for steady state diffusion to derive an expression for the steady state flux from one compartment to another.

45 marks

Question total = 100 marks

Answers

1 (a) *State the first two laws of thermodynamics.*

The internal energy of an isolated system is constant: $dU = dq + dw$; any one of: when two systems are brought into contact, heat flows from the hotter to the cooler body; for any cyclic process, heat cannot be converted completely into work, though work can be completely converted to heat; for any isolated system, entropy increases for any spontaneous process; spontaneous changes are always accompanied by a conversion of energy into a more disordered form; $S = k \ln w$. 5 marks for each law. **10 marks in total.**

(b) *Define the following systems: open, closed, isolated, adiabatic, diathermic.*

Open: matter and all forms of energy can be exchanged

Closed: only energy in all its forms can be exchanged

Isolated: neither energy (of any sort) nor matter can be exchanged

Adiabatic: Only energy as work is exchanged.

Diathermic: Only energy as heat is exchanged.

2 points each, **10 marks in total**

c) Derive an expression for the work done by the system for the isothermal reversible expansion of an ideal gas.

$$work = - \int_{V_1}^{V_2} p(V) dV$$

Sub for p from the ideal gas equation $pV = nRT$.

$$\therefore work = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

For 20 marks

d) *Define constant pressure heat capacity, C_p and derive an expression showing how enthalpy varies with temperature. Clearly state all assumptions.*

C_p is the amount of heat required to raise the temperature by one Kelvin at constant pressure, with no other work than pV work. This heat is therefore the enthalpy (defined from rearrangement of the first law). Words or the equation below are both acceptable for **5 marks** of the **20 marks** total for this question.

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

$$\therefore \int C_p dT = \int_{\Delta H_1}^{\Delta H_2} dH$$

$$\Delta C_p (T_2 - T_1) = \Delta H_{T_2} - \Delta H_{T_1}$$

If C_p does not change (e.g. a narrow temperature range) then the average heat capacity can be substituted. **20 marks**

e) (i) Calculate the enthalpy of reaction

Apply Hess's law, subtracting the sum of the heats of formation of the reactants from the sum of the heats of reaction of the products gives $\Delta H_r^\circ = -2.640 \text{ kJ mol}^{-1}$. **15 marks** for Hess's law, correct arithmetic, significant figures and units.

(ii) Calculate the change in C_p the constant pressure heat capacity for the reaction.

Note that heat capacity is a state function since both enthalpy H and temperature are state functions. A similar formulation to Hess's Law enables calculation of $\Delta C_p = 9.631 \text{ J K}^{-1} \text{ mol}^{-1}$.

15 marks

(iii) Calculate the enthalpy of reaction at 750 K and clearly state all assumptions.

Sub into the equation derived in (d) to get $\Delta H_r^\circ (750 \text{ K}) = 1.713 \text{ kJ mol}^{-1}$ for **10 marks**

2 a) List the principal intermolecular forces in aqueous solution and give their typical energies

Ionic, 250 kJ mol^{-1} ; ion dipole 15 kJ mol^{-1} ; hydrogen bond (O & N e.g alcohols, amines, carboxylic acids, carbonyls); hydrophobic interactions $<40 \text{ kJ mol}^{-1}$; π - π interactions $< 40 \text{ kJ mol}^{-1}$, van der Waals $0.4\text{-}4 \text{ kJ mol}^{-1}$.

20 marks

b) What is the Bjerrum Length? Derive an expression for this variable and calculate its value in pure water at 298.15 K

The Bjerrum length, l_B is the separation of two charges when the Coulomb energy is comparable to the thermal energy per particle, $k_B T$.

Recall the equation for Coulomb energy:

$$u(x) = \frac{q_1 q_2}{4\pi r \epsilon \epsilon_0}$$

Substitute $k_B T$ for the energy $u(x)$, l_B for the distance r , ϵ is the relative permittivity and ϵ_0 is the permittivity of free space. Substitute in the data provided, rearrange to get $l_B = 7.12 \times 10^{-10} \text{ m}$, or around 0.7 nm . This is the same order of magnitude as a bond length and around double the hydrated radius of K^+ .

20 marks

c) A saturated solution of lead (II) chloride, $PbCl_2$ was prepared at 298.15 K. On analysis, the concentration of Pb^{2+} was found to be $15.9 \text{ mmol dm}^{-3}$. Show that this is consistent with the solubility product for $PbCl_2$ being 1.6×10^{-5} .

Write down the definition of the solubility product $K_{sp} = [Pb^{2+}][Cl^-]^2$. There are two moles of chloride produced for each mole of Pb^{2+} . Substituting the observed concentrations gives $K_{sp} = [Pb^{2+}](2[Cl^-])^2 = 0.0159 \times (2 \times 0.0159)^2 = 1.608 \times 10^{-5}$

15 marks

d) Calculate the solubility of lead chloride in water where the initial concentration of Pb^{2+} was 1 mmol dm^{-3} .

Solubility S is the number of moles per dm^3 that dissolve to form a saturation solution.

From the balanced equation, $[Pb^{2+}] = S$, $[Cl^-] = 2(S + 10^{-3})$

Sub into the expression for the solubility product, collect the terms and rearrange to get:

$$S^2 + 10^{-3}S - K_{sp} = 0$$

Solve for S taking the positive root, $S = 0.0158 \text{ mol dm}^{-3}$. **20 marks** for setting up the common ion problem correctly, arithmetic and relevant comments.

e) Define pH acid dissociation constant K_a and pK_a and rank the following acids in order of increasing acid strength:

Substance	pK_a
Acetic acid	4.76
Ascorbic acid	4.17
Phenol	9.95
Benzoic acid	4.20
Hydrogen cyanide	9.21

Which, if any, of these compounds will be in the protonated (un-ionised) forms in pH 7.4 buffer solution. Justify your answer.

$$pH = -\log_{10}[H^+]$$

For the dissociation of a monobasic acid HA:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$pK_a = -\log_{10}K_a$$

10 marks for the definitions.

5 marks for noting that strong acids have small pK_a and correctly ranking the acids in order of increasing strength: phenol, HCN, acetic acid, benzoic acid, ascorbic acid.

Remaining 10 marks for taking logs of the K_a expression (or quoting, or deriving the Henderson Hasselbalch equation to justify the answer that HCN and phenol will be

overwhelmingly present in the protonated forms at pH 7.4 and the remainder will be ionised (2-3 orders of magnitude in all cases).

3 (a) *What are the important properties of a state function?*

If a state function, e.g. $U(x, y)$ is integrated, the integral has a definite value which is independent of the path taken between A and B. dU is an exact differential.

$$\Delta U = \int_A^B dU$$

We can write an exact differential:

$$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy$$

The order of differentiation does not affect the result for the second differential:

$$\frac{\partial^2 U}{\partial y \partial x} = \frac{\partial^2 U}{\partial x \partial y}$$

5 marks each. 15 marks total. Properly notated equations required for full marks.

b) *Is the following equation a state function? Explain your answer*

$$dT = \frac{p}{R} dV + \frac{V}{R} dp$$

Write the total differential of $T(V, p)$:

$$dT = \left(\frac{\partial T}{\partial V}\right)_p dV + \left(\frac{\partial T}{\partial p}\right)_V dp$$

Comparing the two equations:

$$\left(\frac{\partial T}{\partial V}\right)_p = \frac{p}{R} \text{ and } \left(\frac{\partial T}{\partial p}\right)_V = \frac{V}{R}$$

Differentiating the coefficients of dV and dp :

$$\frac{\partial^2 T}{\partial V \partial p} = \frac{1}{R} \text{ and } \frac{\partial^2 T}{\partial p \partial V} = \frac{1}{R}$$

The original expression is therefore an exact differential since the second derivatives of $T(p, V)$ are equal and independent of order of differentiation.

10 marks. Full marks for the exact proof. 4 marks if the answer relies on the fact that all the variables in the original equations are state functions.

Given:

$$U = H - pV$$
$$G = H - TS$$

the first law of thermodynamics and the Clausius relationship:

$$dS = \frac{\delta q_{rev}}{T}$$

(i) Show that:

$$dG = Vdp - SdT$$

Clearly state all assumptions.

3c(i) Starting with the differential form of the first law $dU = \delta q_{rev} + \delta w$ For the first of the fundamental property relationships, assuming reversibility, constant p and only pV work and $w = \int p dV$, so $\delta w = -pdV$. Sub this for work into the first law, and use the Clausius expression to sub for the heat to yield:

$$dU = TdS - pdV. (1)$$

This is now generally true since it consists only of state functions. **10 marks so far**

$$H = U + pV$$

Get the differential for using the product rule:

$$dH = dU + pdV + Vdp (2)$$

Similarly for G :

$$dG = dH - TdS - SdT (3)$$

Sub for dU from (1) in (2):

$$dH = TdS - pdV + pdV + Vdp = TdS + Vdp (4)$$

Sub for dH from (4) into (3):

$$dG = TdS + Vdp - TdS - SdT$$
$$\therefore dG = Vdp - SdT$$

10 marks for the last part

Total 25 marks. Answers must include clear statements of the assumptions (for 5 marks) and maths rules employed.

3(c) (ii) *Derive the Gibbs-Helmholtz equation:*

$$\left(\frac{\partial \left(\frac{G}{T} \right)}{\partial T} \right)_p = -\frac{H}{T^2}$$

showing the temperature dependence of free energy.

Starting with (G/T) and writing down its total differential using the product rule: $(uv)' = u'v + v'u$

Substituting from: $G = H - TS$ (the definition of Gibbs energy) and $dG = Vdp - SdT$

Let $u = G$ and $v = 1/T$

$$\therefore du = dG, dv = -1/T^2 \text{ and } \therefore d\left(\frac{G}{T}\right) = \frac{dG}{T} - \frac{GdT}{T^2}$$

Rearranging gives: $d\left(\frac{G}{T}\right) = \frac{TdG - GdT}{T^2}$. Sub for G and dG to yield: $d\left(\frac{G}{T}\right) = -\frac{H}{T^2}dT + V\frac{dp}{T}$.

Now write down the total differential:

$$d\left(\frac{G}{T}\right) = \left(\frac{\partial(G/T)}{\partial T}\right)_p dT + \left(\frac{\partial(G/T)}{\partial p}\right)_T dp$$

Comparing coefficients for dT gives the Gibbs Helmholtz equation for constant pressure:

$$\left(\frac{\partial(G/T)}{\partial T} \right)_p = -\frac{H}{T^2}$$

For 40 marks

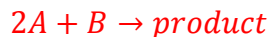
3c(iii) *Show how Gibbs free energy varies with pressure.*

Comparison of the dp coefficients for the second term in the expressions for $d(G/T)$ in **3(c)(ii)** gives the constant temperature result (or solve by substitution ($u = 1/T$ etc) from the result in (c) part (i):

$$\left(\frac{\partial(G/T)}{\partial p} \right)_T = \frac{V}{T}$$

For 10 marks

4 a) Find the integrated rate law for the third order reaction:



Where B is present in large excess so that its concentration does not change significantly during the course of the reaction.

Write down the rate law. Strictly the rate with respect to A should be halved (from the stoichiometry. Not essential of the rate equation is clear.

$$\text{Rate} = -k[A]^2B$$

Since B is kept constant, this is effectively second order. Separation of variable and definite integration from $t = 0$ to $t = t$ and from $[A] = [A]_0$ to $[A]_t$ gives the integrated rate law:

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + k[B]_0 t$$

20 marks

b) Derive an expression for the half-life of the reaction in (b).

For $t = t_{1/2}$ $[A]_t = [A]_0 / 2$. Sub into the above equation to get:

$$t_{1/2} = \frac{1}{k[B]_0[A]_0}$$

10 marks

c) Sulfur dioxide, SO_2 is widely used as a preservative and is an important component of acid rain. Its Henry's Law constant in water at 298.15 K is $1.18 \times 10^{-5} \text{ mol dm}^{-3} \text{ Pa}^{-1}$. The median partial pressure of SO_2 in Beijing is $1.16 \times 10^{-3} \text{ Pa}$.

(i) Calculate the aqueous concentration of sulfur dioxide in rainwater in Beijing.

Recalling the definition of Henry's Law constant:

$$K_H = \frac{[\text{gas(aq)}]}{p_{\text{Gas}}}$$

Sub in the data, rearrange to get the concentration = $1.37 \times 10^{-8} \text{ mol dm}^{-3}$.

10 marks

(ii) Sulfur dioxide reacts in water according to the reaction below:



The pK_a of this reaction is 1.81. Predict the pH of the rainwater. Make all your assumptions clear.

Write down an expression for the acid dissociation constant:

$$K_a = \frac{[H^+][HSO_3^-]}{[SO_2(aq)]}$$

Note that $[SO_2]$ will remain constant due to the large reservoir and the relatively small dimensions of the raindrop. Sub in the concentration calculated above, note that the proton concentration will be equal to the conjugate base concentration. Assumptions that there are no other acidifying gases (a poor assumption) and that only the first dissociation need be considered (OK). If x is the concentration of protons and conjugate base:

$$K_a = \frac{x^2}{[SO_2(aq)]}$$

and $K_a = 0.0155$, solve for x to yield $x = 1.457 \times 10^{-5} \text{ mol dm}^{-3}$ and the pH is therefore = 4.84.

15 marks

d) Two large volume well-stirred solutions of glucose are separated by a permeable membrane of thickness h such that the concentrations in the solution remain homogeneous. The concentrations of glucose in the two compartments are c_1 and c_2 where $c_1 > c_2$. The partition constant for glucose dissolving in the membrane is given by:

$$K = \frac{c_{mem}}{c_{sol}}$$

Where c_{mem} is the concentration of the glucose in the membrane and c_{sol} is the concentration in solution (i.e. c_1 on one side and c_2 on the other side). The diffusion coefficient for glucose in the membrane is given by D . Fick's second law of diffusion in one dimension is:

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2}$$

Solve this equation for steady state diffusion to derive an expression for the steady state flux from one compartment to another.

Since steady state diffusion is specified:

$$\frac{d^2c}{dx^2} = 0$$

Integrate w.r.t. x :

$$\frac{dc}{dx} = A$$

where A is a constant of integration.

Integrate again w.r.t. x :

$$c(x) = Ax + B$$

where B is another constant of integration.

Use the boundary conditions to evaluate A and B . When $x = 0$, $c = Kc_1$ so $B = Kc_1$.

When $x = h$ the concentration is Kc_2 .

$$\therefore A = \frac{Kc_2 - c_1}{h}$$

Sub the expressions for the constants into the expression for $c(x)$:

$$c(x) = \frac{Kc_2 - c_1}{h}x + Kc_1$$

Differentiate w.r.t. x to get the concentration gradient:

$$\frac{dc}{dx} = \frac{Kc_2 - c_1}{h}$$

Fick's first law:

$$J = -D \frac{dc}{dx}$$

Sub for concentration gradient to get the steady state flux through the membrane:

$$J = -D \frac{Kc_2 - c_1}{h} = -DK \frac{\Delta c}{h}$$

Flux will therefore depend on the material properties of the membrane (diffusion coefficient, partition coefficient), the concentration difference and inversely on the membrane thickness.

45 marks