

Indian Institute of Science Education and Research (IISER) Kolkata
CH5104: Principles of Physical Chemistry
End-Semester Examination

Full marks – 50

Time – 180 minutes

27 November 2018

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- Do not adopt any unfair mean.
 - Attempt ALL the questions. Answer all parts of a question together.
 - Do not use mobile phone for calculation. Use your own calculator.
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1. Consider an electrochemical reaction $O + e \leftrightarrow R$ followed by a chemical step $R \rightarrow \text{Product}$.
- (a) The electrochemical step has a mixed kinetic and diffusion control where diffusion is the rate determining step accompanied by a large charge transfer resistance. Draw the equivalent circuit and the Nyquist plot, labeling the parameters. (2)
- (b) What are the controlling factors (at least 4) of the double layer capacitance of this electrode? (2)
- (c) If electrochemical charge transfer kinetics is slow, the Tafel slope will be small or large? Why? (1)
- (d) If the rate of chemical step is slower than voltage scan rate, draw the cyclic voltammogram. (1)
- (e) If the electrode is made of a semiconductor (SC) and another SC is attached to it, demonstrate with a diagram the photoelectrocatalysis for water splitting at the SC-SC interface. (2)
2. (a) Show band bending at the interface between (i) p-doped silicon and electrolyte, and (ii) n-type TiO_2 and electrolyte. The potential at the photoelectrode surface is negative in both cases. Explain with diagram. (1.5+1.5)
- (b) Write the expression and explain the terms of the rate of formation of charge carriers at a distance x from the semiconductor electrode/solution interface. (2)
- (c) Show and explain the band bending of n-type semiconductor in contact with the electrolyte, in the presence of low concentration of surface states in the semiconductor. (2)
- (d) How the band bending in (c) will alter when ion adsorption increases? (1)
3. (a) What do you understand by absorption coefficient and absorption depth? (2)
- (b) Differentiate between Shockley-Read-Hall recombination and Auger recombination. (2)
- (c) In a p-n junction show the directions of electron diffusion, electron drift, hole diffusion and hole drift. (2)
- (d) Show the operation of a p-n junction diode in the dark under reverse bias. (1)
- (e) In a p-n junction under light illumination illustrate and explain the consequences under open-circuit and short-circuit conditions. (2)
4. (a) Comment on the significance of non-linear optical methods. (2)
- (b) Explain the concept of second harmonic generation (SHG). (2)
- (c) What is the principal instrumental requirement for SHG? (1)
5. (a) Briefly explain sum-frequency generation. (3)
- (b) What is the function of an optical parametric oscillator (OPO)? Explain. (4)
6. State the method of determination of the radius (w_0) of a diffraction-limited spot. (3)
7. (a) What is the basic principle of action of a pump-probe experiment? (4)
- (b) Draw a schematic diagram of ns-laser flash photolysis spectrometer. (2)
8. State mathematically how signal for transient absorption (TA) spectroscopy is derived from measuring the probe pulses. (4)

