Remind: The answer of this exam should be provided in English in order to protect the right of the student, answering in non-English language will not be considered for grading. The answer should be provided in form of short essay, i.e. a **clear answer** and the **justification of the answer** should be provided simultaneously. **NONE OF THE QUESTIONS IN THIS EXAM REQUIRE A NUMERICAL ANSWER**

CO_2 reduction reaction (CO_2RR) has gained significant interest in the fields of green chemistry and renewable energy due to the advantage of simultaneously converting the greenhouse gas CO_2 into organic substances that can be used as starting material for further organic synthesis. In this regard, the catalysts that can effectively reduce the reduction potential are central. Among all of the candidates, copper and its related oxide species are reported as a special system, since, under certain circumstances, they can reduce the CO_2 into two-carbon products such as ethanol, which are the most valuable products from industry perspective. Therefore, how exactly the reaction mechanism can be determined and further manipulated is of great interest to the scientists.

As the electrochemical reduction is often carried out on a solid/liquid interface, CO_2 gas is often firstly dissolved into aqueous solution. The dissolution of CO_2 gas may undergo two different pathways, 1) reacts with water and then converts into carboxylic acid or 2) dissolves into water in form of gas.

A) For pathway 1, please suggest what kind of aqueous solution exhibits the highest capacity to dissolve CO_2? Please provide your reason **(2 pts)**

Imagine now that, based on your answer to question (A), pathway 1 conditions have been found that result in optimal CO_2 concentration in water. For pathway 2, increasing partial pressure of gas phase CO_2 (pCO_2) is a simple way to increase solubility.

B) Build a mathematical expression which relates pathway 1 conditions to the pCO_2 necessary to achieve the same solubility via pathway 2. Assume ideal gas and solution conditions. Hint: To justify your choice of equations, take into account that carbonic acid is a weak acid and that formation of carbonic acid from CO_2 and water is endergonic. **(10 points).**

For pathway 2, it is very challenging to evaluate whether the CO_2 molecules remain as microscopic bubble or free single molecule in the solution. A recent study carried by Li *et al.*(J. Li, J. Guo, H. Dai, *Sci. Adv.* **2022**, 8,19, 399) provides a strategy to resolve this question by using their newly developed microscale infrared spectroscopy.

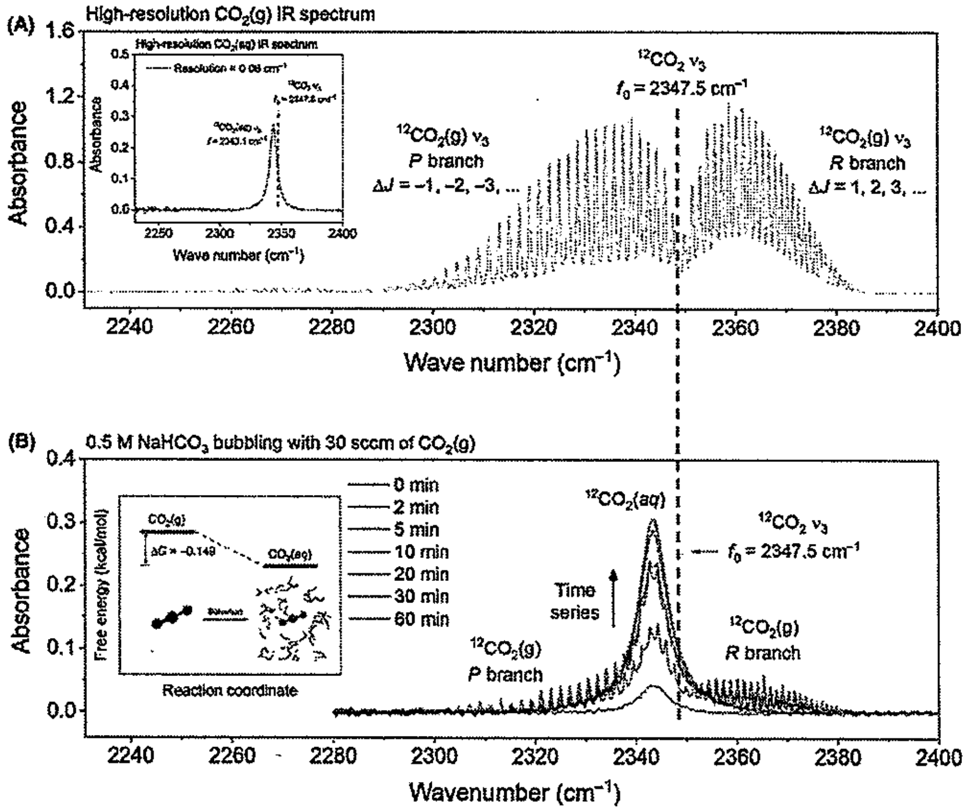

*Fig. 1 This figure is modified from Li et al.'s research (cite). **(A)** High-resolution absorption IR spectrum of gas phase CO₂ and CO₂ in solution phase as inset figure. **(B)** Time-resolved IR spectrum acquired at different timing during experiment of bubbling gas phase CO₂ into a 0.5 M NaHCO₃ solution (peak intensity from low to high as indicated by the arrow). Inset shows the thermodynamics of CO₂ solvation*

As shown in **Fig. 1**, the authors claim that during the bubbling of the CO_2 gas, the CO_2 is initially in form of gas in the solution, about 20 min after, the CO_2 is mainly in form of dissolved molecule hydrated by water. This conclusion is based on the observation of the spectrum feature change in **Fig. 1(B)**, where the early stage spectra show more significant spiky feature than the late-stage spectra.

C) Please provide an explanation of why gas phase CO_2 absorption spectrum looks so different from the solvent hydrated CO_2 spectrum in **Fig. 1(A)**? What is the absorption peak at 2347.5 cm^{-1} and what are the spiky features? **(3 pts)**

D) Do you consider the mentioned IR spectroscopy a suitable method to perform quantitative characterization of the amount of dissolved CO_2, and why? Please also provide another technique that may help you with characterizing the CO_2 concentration in your solution, please also briefly provide your reason. **(5 pts)**

A surprising conclusion from the Li et al. study is that pathway 2 CO_2 solubilization is exergonic (Fig. 1B, inset). Meanwhile, the solubilization of other biologically relevant gases, such as O_2 or N_2, is endergonic.

Based on your knowledge of physical chemistry and their molecular structures **(E)** provide a thermodynamic explanation for why CO_2 solubilization is exergonic compared to the other two gases **(5 pts)**. **(F)** Hypothesize if CO_2 solubilization is entropically or enthalpically driven. Justify your answer **(5 pts)**. **(G)** What effect would raising the temperature have on CO_2 solubilization? Justify your answer **(5 pts)**

To perform the CO_2RR, you try to set up a three-electrode system to measure the cyclic voltammogram (CV) scanning from anodic region to cathodic region,

H) please provide a reason for why it is necessary to use a three-electrode system instead of two-electrode system. **(5 pts)**

Under your experimental condition, it is crucial to select a stable reference electrode so that it can guarantee the validity of the voltage application.

I) Please discuss which reference electrode will fit best to perform this experiment? **(5 pts)**

For the working electrode, you now have three candidates: gold foil, carbon paper and copper foil. You discover that the measured overpotential for CO_2RR in your CV scan shows that the carbon paper is the highest, followed by gold and then copper,

J) please provide a hypothesis to explain this trend. **(5 pts)**

In 1992, Rudolph Marcus was awarded the Nobel Prize for developing a simple and elegant theory to explain the kinetics of electron transfer (ET). Marcus theory is a direct extension of the Arrhenius general treatment of reaction kinetics, which states that the reaction rate constant at any temperature T depends on (a) the pre-exponential constant A, and (b) the activation energy E_a.

According to Marcus theory, E_a depends on the standard Gibbs free energy change of ET (ΔG_{ET}^{o}) and the reorganization energy λ_0 via the expression $E_a = \frac{(\lambda_0+\Delta G_{ET}^{o})^2}{4\lambda_0}$. Here, Marcus interpreted λ_0 as the energy cost to re-arrange the structure of the donor-acceptor-solvent complex from its reactant configuration to its product configuration. Based on this brief description and your own knowledge, please answer the following questions:

K) Assume that, on average and for all three electrodes (C, Au, Cu), the CO_2RR half reaction (CO_2 + electrons + protons → reduced carbon products) standard reduction potential remains constant and requires a constant number of electrons and protons. What is the minimum non-zero Ea that the CO_2RR can have with each electrode as a function of the electrode reduction potential? **(5 pts)** Hint: This question is the first step in solving question (L)

L) Based on your answer to questions (J) and (K), which of the three electrodes (Au, C, or Cu) induces a reactant configuration that is the most similar to the product configuration? Assume that all reactions have their minimum non-zero activation energies as determined in (K) **(5 pts)**

Marcus' key insight was to model the electronic structure of both the reactant and product pair as two parabolas ($y = ax^2 + 2abx + b^2 + c$) where x is the electron transfer reaction coordinate, and y the energy of the system. The intersection between the two

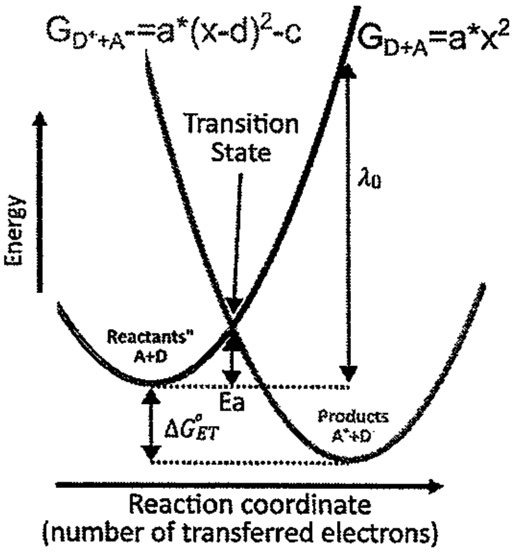

Fig. 2. The determining factors of electron transfer kinetics, according to Marcus theory. Parabolas represent electronic configuration model of reactant (D+A, black) and product (D^++A^-, blue) pairs. Red line represents the standard energy diagram for a reaction. a, d and c are characteristic constants of the Marcus model. Other abbreviations are as described in the exam text.

parabolas thus represents the cross-over point, or the location of the transition state (Fig. 2).

M) Please provide a quantum mechanical justification for why the electronic structure ("Aufbau") of any molecule/atom can be modeled by such a parabolic equation **(5 pts).**

The electrochemical experiment is performed within a flow-cell where the reaction products can be analyzed simultaneously as the reaction carries on. You direct the exit flow into two different post analysis systems: GC-MS and ICP-MS.

N) For the two MS systems, which one can be used to determine the organic reduction products? Please provide a brief working principle explanation of the two systems to justify your answer. **(5 pts)**

Interestingly, you also discover that a trace amount of copper is dissolved into the solution that can be detect by the MS. To be able to acquire the exact concentration of the dissolved copper species,

O) how would you perform the concentration calibration for the MS? You may start from using the standard copper solution with known concentration. **(5 pts)**

The flow cell is designed in a way that an FT-IR or a Raman system can be installed at the backside of the working electrode, so that you are able to acquire the vibration spectrum in parallel to the ongoing electrochemical CO_2RR. Based on the MS result, you are suspecting that a carbonate-copper complex intermediate is formed during the reaction, which further causes the dissolution of the copper in the later process. As such, you are seeking for the evidence of the formation of Cu-O bond by using either FT-IR or Raman.

P) Please briefly explain the principle of two mentioned techniques, and if you have only a green 532 nm LASER light source in your hand, which setup can be constructed? Assuming you have the availability of all the other optics. Please illustrate the instrumental design including: light source, objective, dichroic mirror, spectrometer and detector. **(5 pts)**

Thanks to infrared telescopes, crystalline substances in space (in asteroids or comets) can be detected via vibrational spectroscopy. Because temperature in space is close to absolute zero, it has become necessary to calculate 0 K vibrational spectra.

Q) Explain why, according to the third law of thermodynamics, such a calculation is impossible and why quantum mechanics predicts that it is possible. **(5 pts)**

From the vibrational spectroscopy, you discover the Cu-O vibration mode presents even in your pristine sample, where no carbonate is introduced. Therefore, you start to wonder whether your copper substrate is already oxidized before you conduct the experiment. To verify your concern, you send both the as-prepared and after CO_2RR experiment copper substrate into SEM to characterize the morphology change. Comparing to other optical techniques,

R) please shortly explain the reason of why SEM is able to provide high spatial resolution in nanometer scale? Please discuss the fundamental physics using Abbes Diffraction Limit. **(5 pts)**

In your SEM results, you discover the formation of many nanocubic-like structure on your substrate after the CO_2RR experiment, which makes you suspect the formation of Cu_2O crystal. To identify the nano crystal, you are considering of using XRD to perform structural characterization.

S) Please provide a brief explanation of why XRD can be used to identify the crystal structure with discussing the correlation between diffraction pattern and the crystal lattice structure. **(5 pts)**

Single crystal diffraction patterns are characterized by discrete points of light on the detection surface (Fig. 3) called "reflections".

T) Explain why crystals do not induce continuous diffraction. In other words, what is the physical basis for each reflection possessing a characteristic diffraction angle θ or, equivalently, Miller index (hkl)?

(5 pts) Hint: mirror planes are a geometrical construction, and not physically present within the crystal lattice.

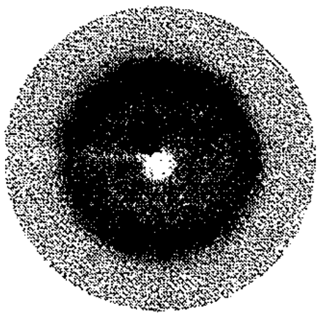

Fig. 3 A typical diffraction pattern

Supporting Information:

- *Abbreviations:*

Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS); Gas Chromatography-Mass Spectroscopy (GC-MS); Cyclic Voltammetry (CV); Fourier Transform Infrared Spectroscopy (FT-IR); Scanning Electron Microscopy (SEM); X-ray Diffraction (XRD); Light Amplification by Stimulated Emission of Radiation (LASER).

- *Equations:*

Thermodynamics

Perfect gas state function: $pV = nRT$

Boltzmann equation: $p_i = \frac{1}{Q} e^{-\frac{\varepsilon_i}{kT}}$

Boltzmann entropy: $S = kln(W)$

Hess' law: $\Delta H_r^o = \sum_P^i \nu_i \Delta H_{fi}^o - \sum_R^j \nu_j \Delta H_{fj}^o$

Gibbs Free energy change equation: $\Delta G = \Delta H - T\Delta S$

Gibbs free energy of a compressible substance vs. pressure: $G_{m,f} = G_{m,i} + RTln(\frac{p_f}{p_i})$

Gibbs free energy of a substance vs temperature: $G_{m,f} = G_{m,i} - S_m(T_f - T_i)$

The Clapeyron Equation: $\frac{dp}{dT} = \frac{\Delta H_{m,trs}}{T_{trs}\Delta V_{m,trs}}$

The Clausius- Clapeyron Equation: $\frac{dp}{dT} = \frac{P\Delta H_{m,trs}}{T_{trans}^2 R}$

The Chemical potential of a gas: $\mu_j = \mu_j^o + RTln(p_j)$

The Chemical potential of a liquid at phase equilibrium: $\mu_{A(liquid)} = \mu_{A(gas)}^o + RTln(p_{A(gas)})$

The Chemical potential of a solvent: $\mu_j = \mu_j^* + RTln(x_j)$

Raoult's law: $p_j = x_j p^*$

The Chemical potential of a solute (as a function of concentration): $\mu_k = \mu_k^o + RTln([k])$

Henry's law (as a function of concentration): $[k] = K_H p_k$

The reaction Gibbs free energy change (II): $\Delta G_r = \Delta G_r^o + RTln(Q)$

The standard reaction Gibbs free energy change: $\Delta G_r^o = -RTln(K)$

The van't Hoff Equation: $\frac{\Delta H_r^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = ln\left(\frac{K_2}{K_1}\right)$

The Henderson-Hasselbach equation: $pH = pK_a - log_{10}(\frac{[AH]}{[A^-]})$

The Nernst equation: $E_{cell} = E_{cell}^o - \frac{RT}{nF} lnQ$

The Cell potential: $E_{cell} = E_{cathode} - E_{anode}$

Relation between Gibbs free energy and cell potential: $\Delta G_r = -nFE_{cell}$

The reaction potential: $E_r = E_{oxidant} - E_{reductant}$

Relation between Gibbs free energy and reaction potential: $\Delta G_r = -nFE_r$

Kinetics

The Arrhenius equation: $k = Ae^{\frac{-E_a}{RT}}$

Eyring equation: $k = \kappa \frac{k_b T}{h} e^{\frac{-\Delta^0 G^\ddagger}{RT}}$

Marcus variant of the Eyring equation: $k_{ET} \propto e^{-\beta r} e^{\frac{-Ea}{RT}}$

Marcus equation for the activation energy: $E_a = \frac{(\Delta_{ET} G^\circ + \lambda)^2}{4\lambda}$

Quantum mechanics

De Broglie relation: $\lambda = \frac{h}{mv}$

Uncertainty principle: $\Delta x \Delta p \geq \frac{1}{2}\hbar$

Solutions to the Schrödinger equation

Energy of a shell: $E_n = -hcR\frac{Z^2}{n^2}$ with n=1,2,3... principal quantum number

Energy of a subshell/orbital: $E = l(l+1)\frac{\hbar^2}{2I}$

with $l = n - 1$ orbital momentum quantum numbers $(l \leq n)$

and $m_l = 2l + 1$ magnetic quantum numbers $(-l \leq m_l \leq l)$

Energy of a harmonic oscillator: $E = \hbar\omega l\left(n + \frac{1}{2}\right)$ where $n \geq 0$

Principles of diffraction:

Laue conditions: S*a=h, S*b=k, S*c=l

Diffraction intensity of a reflection S produced by a crystal composed of t*u*v unit cells with unit cell diffraction intensity F(S):

$K(S)_{t,u,v} = F(S)_{0,0,0} \sum_{t=0}^{n_1} e^{2\pi i * t * a * S} \sum_{u=0}^{n_2} e^{2\pi i * u * b * S} \sum_{v=0}^{n_3} e^{2\pi i * v * c * S}$

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