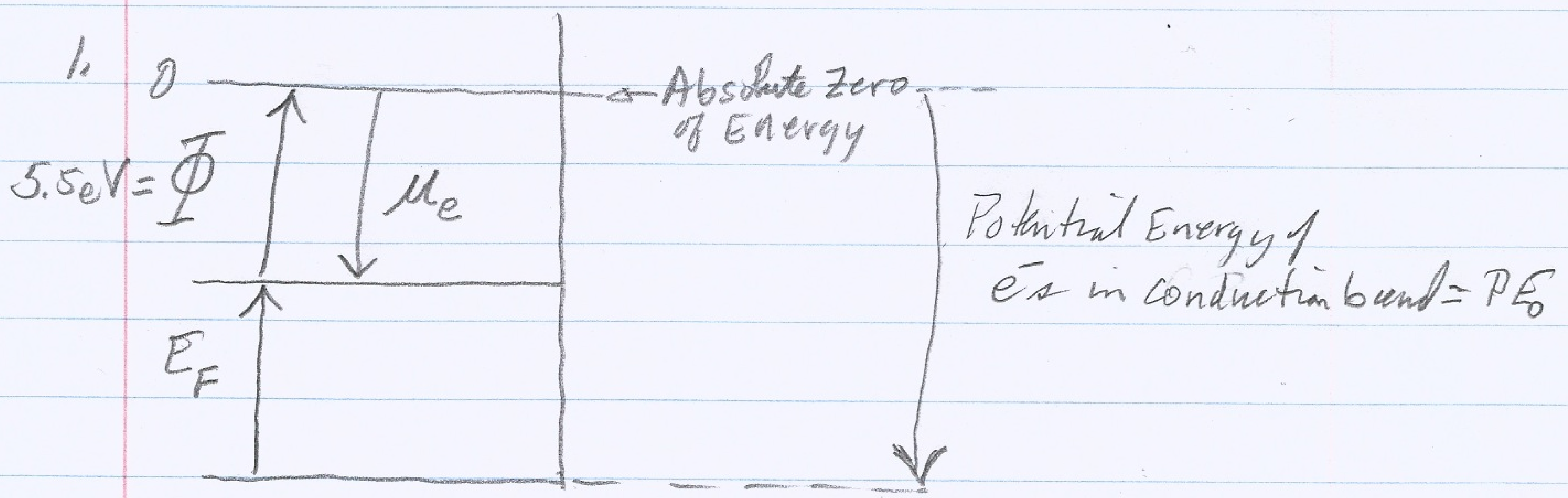
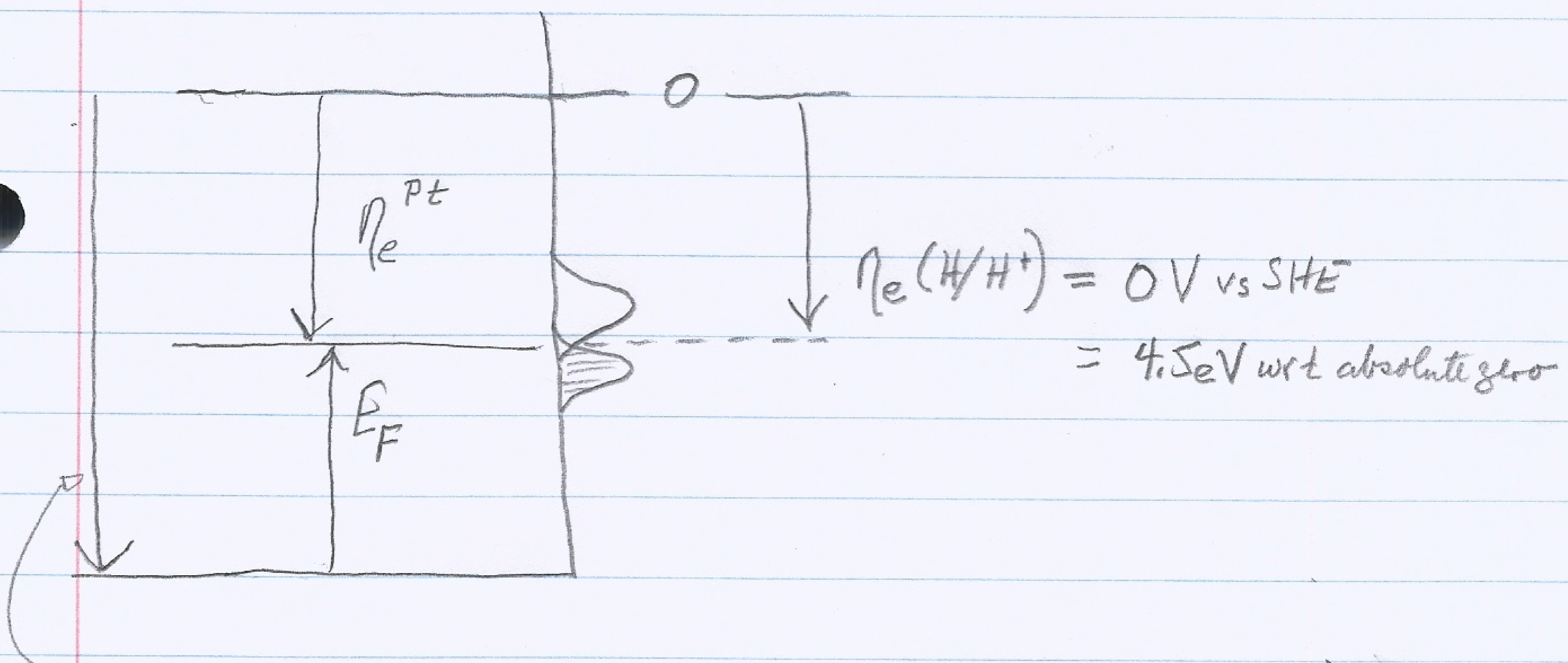
# MSE 112

## Solutions to Midterm Exam

1.





Potential Energy of $e^-$ in conduction band $= PE_0 + \frac{(5.5-4.5)eV}{e}$

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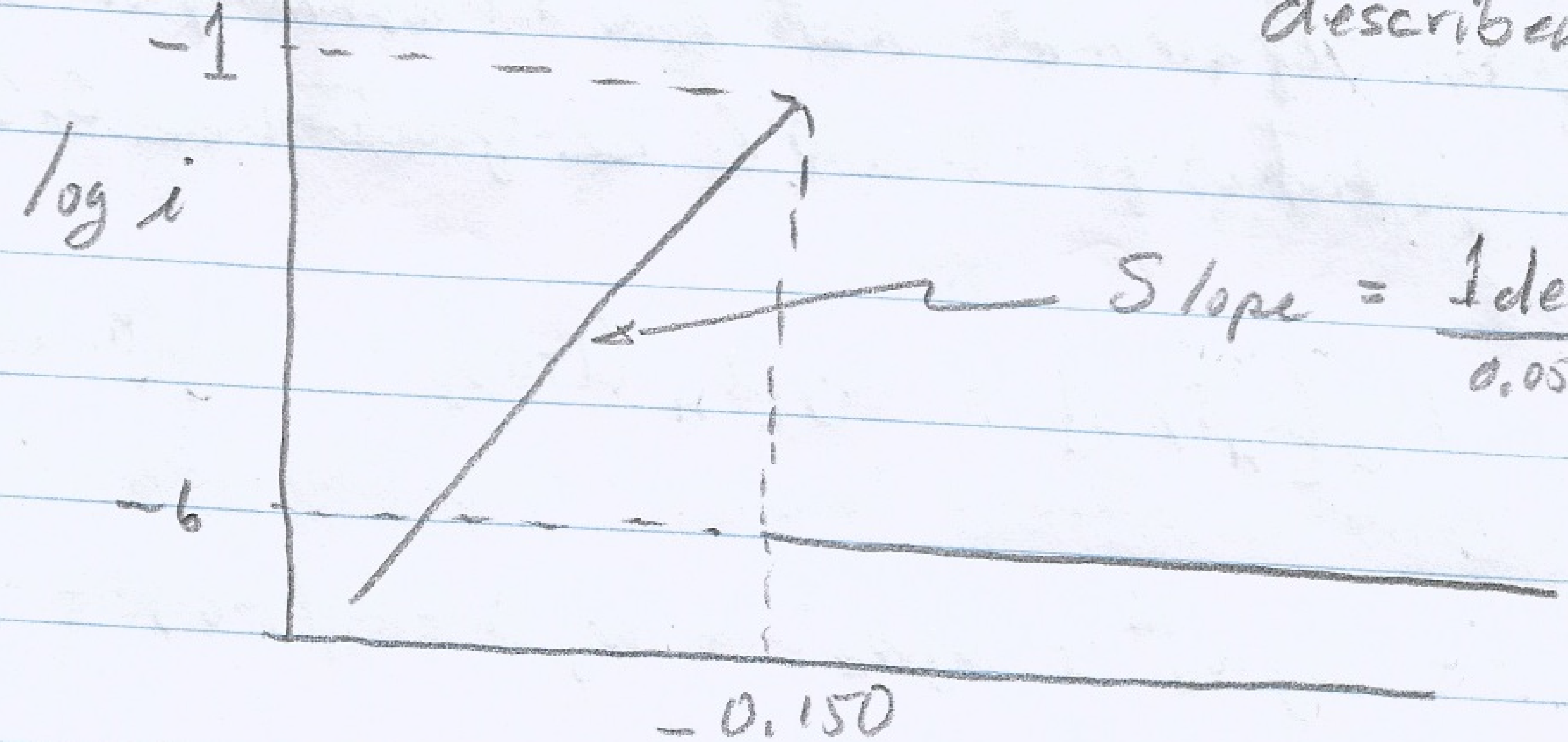
2. Oxidation Reactions:

(i) Based on the information provided: The oxidation of Ti is described as follows:

⑤



$$\text{Slope} = \frac{1\ \text{decade}}{0.050\,V} = 20\,V^{-1}$$

(ii) Since Pd is a noble metal its oxidation is negligible

Reduction reactions:

Assuming complete dissociation of 0.5M $H_2SO_4$, the $H^+$ concentration is $1M \Rightarrow pH = 0$

$$\therefore \Delta\phi_e(H) = \Delta\phi_e^\circ(H) - \frac{.0592}{2}\log\frac{(P_{H_2}=1\,atm)}{[H^+]=1} = 0\,V$$

(i) For $H^+$ reduction on Ti:

$$\log i_o = m\,\Delta\phi_e + b$$

$$\log(10^{-9}) = \left(\frac{1}{0.052}\right)(0V) + b$$

$$\Rightarrow b = -9$$

⑩

$$\therefore \log i = -\frac{1}{0.052}\Delta\phi - 9$$

(ii) For $H^+$ reduction on Pd

$$\log i_o = m\,\Delta\phi_e + b$$

$$\log(10^{-6}) = \frac{1}{0.024}(0) + b$$

$$b = -6$$

⑩

$$\therefore \log i = \frac{1}{0.024}\Delta\phi - 6$$

Thus, the corrosion potential of Ti is raised to 0V. When the Ti is galvanically coupled to Pd with an area ratio of

$$\frac{A_{Pd}}{A_{Pd}+A_{Ti}} = 0.056.$$

⑤ Adding $O_2$ to the acidic solution would most likely passivate the Ti.

Note: a corrosion rate of 10 μm/yr is equivalent to

$$10\times10^{-4}\,\frac{cm}{yr}\;\frac{yr}{365\,days}\;\frac{day}{24\,hr}\;\frac{hr}{3600\,s}\;\frac{4.5\,gm}{cc}\;\frac{Mole}{47.9\,g}\;\frac{3\,equiv}{mole}\;\frac{96{,}500\,coul}{equiv}$$

≅ density of Ti

atomic wt of Ti

$$= 8.6\times10^{-7}\,\frac{amps}{cm^2}$$

$i_{passive} = 10^{-6}$ amps/cm²

⑤ Therefore, to insure that the corrosion rate of Ti is below $\simeq 8.6\times10^{-7}$ amps/cm², the titanium should be in the passive state.

The fraction of the surface area of Pd, $\gamma$, is determined by the requirement that the reduction of $H^+$ at a potential of $-0.150V$ be greater than $0.1 A/cm^2$

$$\therefore \quad \log\left[(i_H^{Pd})\cdot\gamma\right] + \log\left[i_H^{Ti}(1-\gamma)\right] = \log(0.1A)$$

$$\therefore \quad \log i_H^{Pd} + \log i_H^{Ti} + \log\gamma + \log(1-\gamma) = -1$$

$$\log i_H^{Pd} = -\frac{1}{0.024V}(-0.150V) - 6 = 0.25$$

$$\log i_H^{Ti} = -\frac{1}{0.052}(-0.150) - 9 = -6.1154$$

$\Rightarrow$ the current associated with the reduction of $H^+$ on Ti at $-0.150V$ is negligible compared to that of Pd.

$\therefore$, assuming that all of the reduction occurs on Pd would require

$$\log\left[(i_H^{Pd})\gamma\right] = -1$$

$$\therefore \quad 0.25 + \log\gamma = -1$$

⑩ $\log\gamma = -1.25$

$$\Rightarrow \gamma = 0.056$$

The effect of galvanically coupling Pd to Ti is to drive the corrosion potential of Titanium into the passive region

$\Rightarrow i_{corr} = 1\times10^{-6} A/cm^2 \Rightarrow i(H) = 1\times10^{-6} A/cm^2$

⑤ $\therefore \log(1\times10^{-6}) = -\frac{1}{0.024}(\Delta\phi_{corr}) - 6$

$$\Rightarrow \Delta\phi_{corr} = 0 \, V_{SHE}$$

③ (i) To maximize dezincification — that is, the preferential oxidation of Zn — the aqueous solution should be oxygen free so that Copper is thermodynamically stable.

⑩

(ii) Next, the oxidation of Zinc should yield a water-soluble product rather than a solid oxide or hydroxide, which might form as a solid surface film that would slow down the oxidation of zinc

⑤

The possible soluble oxidation products of Zn are $Zn^{++}$, which forms in acidic solutions, and $HZnO_2^-$ and $ZnO_2^{=}$, which form in alkaline solutions.

(iii) Referring to the Pourbaix diagram of Zn, the thermodynamic driving force for the oxidation of Zinc at a particular value of pH is given by the difference in the equilibrium potential of H, which is line ⓐ in the Pourbaix diagram, and the equilibrium potential of Zn which is given by line ⑤ for acidic solutions, and lines ⑩ and ⑪ for alkaline solution.

⑩

A greater thermodynamic driving force is provided by the oxidation of Zn in an acidic solution, and the maximum value is achieved in a solution of $pH = 0$ for the case in which pH is restricted to $0 \leq pH \leq 14$.

⑤

Thus, the values of pH and dissolved oxygen concentration are both 0.