E45 Fall 2011
Solutions to Exam #2

1. (a.) IP is the work (energy) required to remove the highest energy electron from an atom and to move the electron to infinity.

5pts

(b.) When atoms are close enough, the electrons, especially the outer shell electrons, feel the attractive Coulombic forces of the nuclei of neighboring atoms. If the forces are large enough the outer shell electron(s) are removed from the atom and form "free electrons" in the crystal. Metals, by definition, exhibit metallic bonding, which is made possible by the metal's high concentration of free electrons.

10pts. for either

Stated in terms of energy rather than forces, a high concentration of free electrons are present in a crystal composed of closely spaced atoms that have a low IP so that relatively little energy (work) is required to remove the outer shell electrons.

2. (a.) The energy of electrons at the very top of the conduction band of a one dimensional metal in which the potential energy of all conduction electrons is a constant throughout the crystal is $\frac{h^2}{8ma^2}$, where a is the interatomic spacing and m is the mass of an electron.

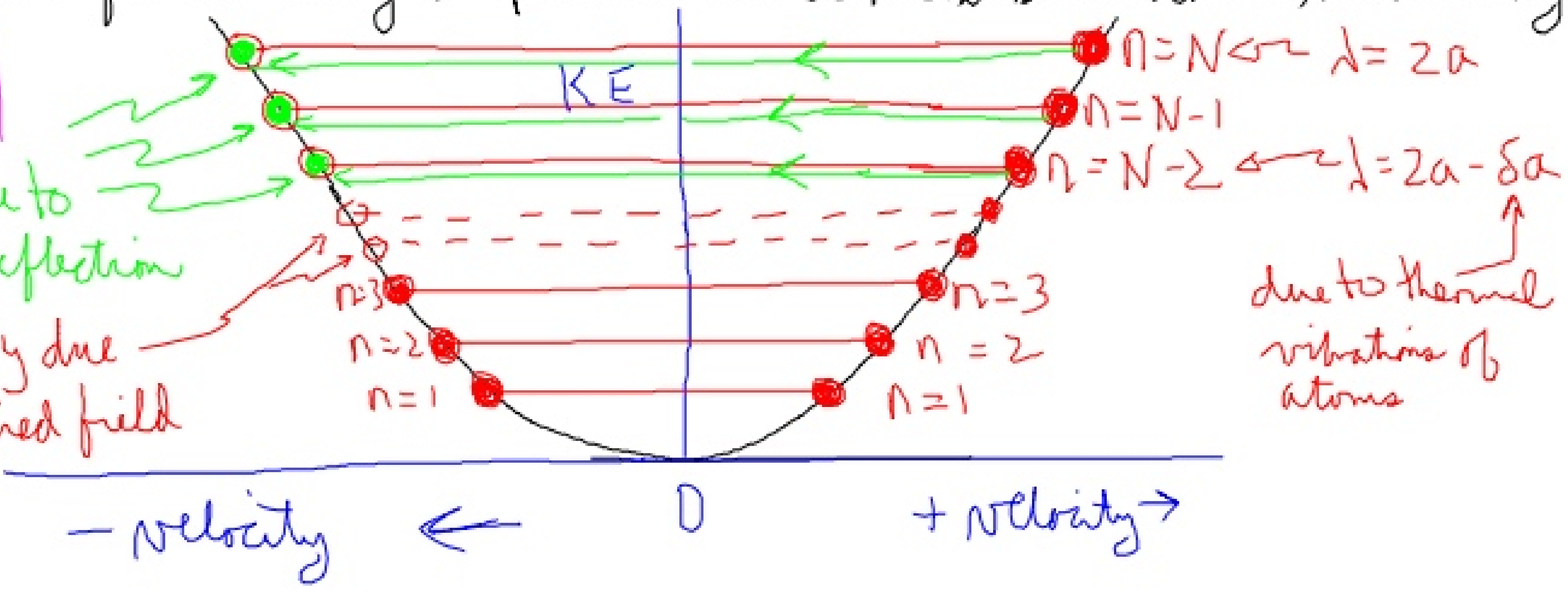
The wavelength of the electrons (maximum of 2) that occupy the highest energy level of the conduction band is: $\lambda_{min} = 2a$.

As temperature increases the amplitudes of the atomic vibrations increase so that the interatomic spacing varies from a minimum of $a - \Delta a_{max}$ to a maximum of $a + \Delta a_{max}$

As a consequence of the thermal vibrations, electrons moving under the influence of an applied electric field and with wavelengths in the range of $2a \pm \Delta a_{max}$ are back reflected

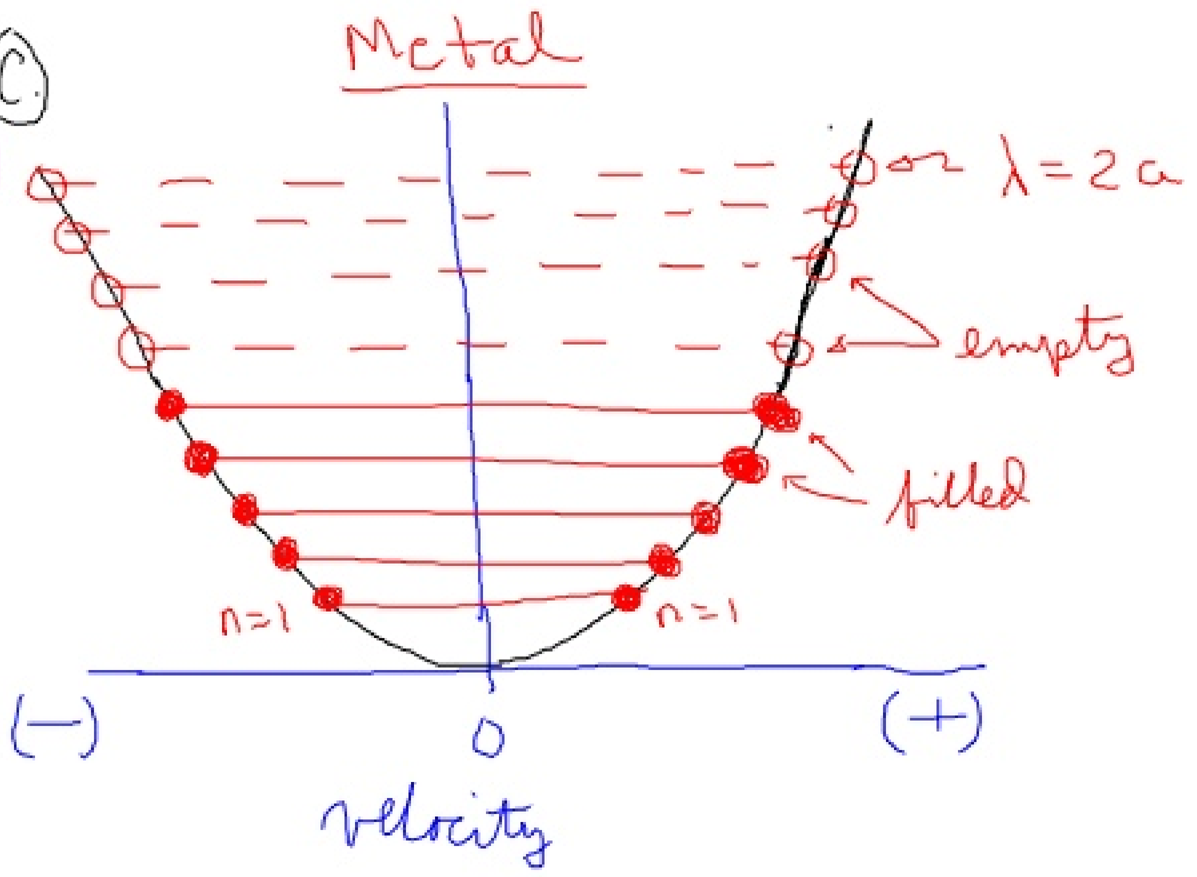
7 pts. for either this or the Figure

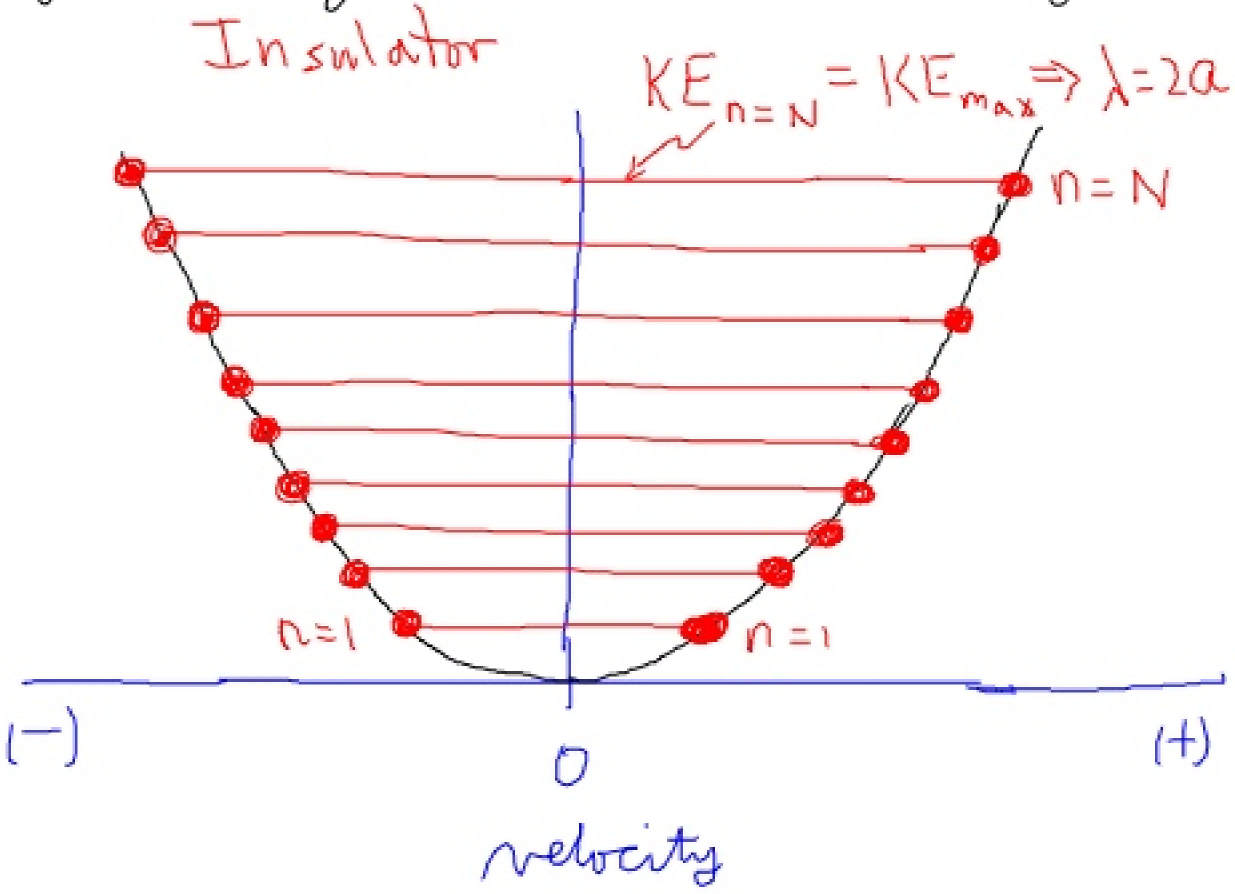
Off crystal planes and sent traveling in the opposite direction, effectively increasing the electrical resistance. A greater number of wavelengths are back reflected as the temperature increases because Δa_{max} increases with increasing temperature. The effect of increasing temperature on a metal's electrical resistivity is described in the figure in which multiple wavelengths are backscattered.



(b.) 6pts The interatomic spacing increases in the vicinity of a vacancy, so that more wavelengths are back-scattered, thereby increasing the electrical resistivity.

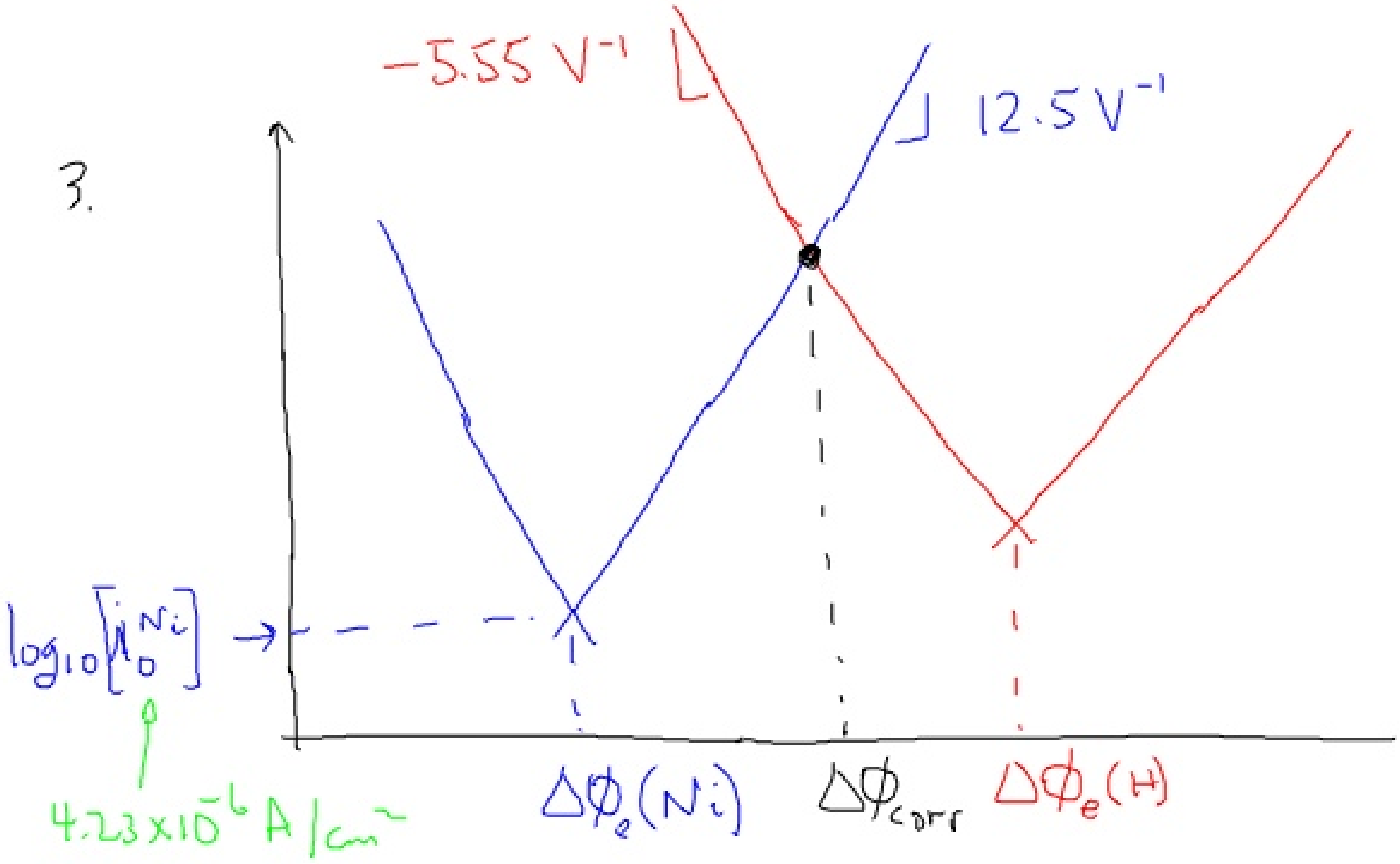
(c.) 12pts





In an insulator, all energy levels are filled so that electrons cannot increase their velocity in the direction of the applied electric field.

3.



5pts. $$\Delta\phi_e(Ni) = \underbrace{-0.230V}_{\Delta\phi_e^0(Ni)} - \frac{0.059V}{2}\log_{10}\frac{\cancelto{1}{[Ni]}}{\underbrace{[Ni^{++}]}_{10^{-5}M}} = -0.378\ V$$

5pts. $$\Delta\phi_e(H) = \underbrace{0V}_{\Delta\phi_e^0(H)} - \frac{0.059}{2}\log\frac{P_{H_2}^{\leftarrow 1atm}}{\underbrace{[H^+]^2}_{1M}} = 0\ V$$

All of the above is the information provided. The objective is to determine i_{corr}^{Ni}.

5pts. $$\log_{10}\frac{i_{corr}^{Ni}}{i_0^{Ni}} = \frac{12.5}{V}\left[\Delta\phi_{corr}^{Ni} - \Delta\phi_e(Ni)\right]$$

$$\therefore \log\frac{i_{corr}}{4.23\times10^{-6}} = \frac{12.5}{V}\left[-0.05V-(-0.378V)\right]$$

$$\log i_{corr} + 5.374 = 4.1$$

$$\log i_{corr} = -1.274$$

5pts. $$\therefore i_{corr} = 53\frac{mA}{cm^2}$$

4. (a) Na^+ and Cl^- are thermodynamically stable so they are excluded from further consideration.

Zn in air-free 1M NaCl (pH 4)

Electrochemical reactions on the surface of Zn:

1pt. $Zn \rightarrow Zn^{++} + 2e^-$

1pt. $Zn^{++} + 2e^- \rightarrow Zn$

1pt. $2H^+ + 2e^- \rightarrow H_2$

1pt. $H_2 \rightarrow 2H^+ + 2e^-$

Note on Grading: Just need to list the reactions. No comments are required.

(b.) Pt in air-saturated 1M NaCl (pH4)

1pt. $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

1pt. $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$

} reactions occuring at the highest rates

1pt. $2H^+ + 2e^- \rightarrow H_2$ } reaction occurring at very low rate

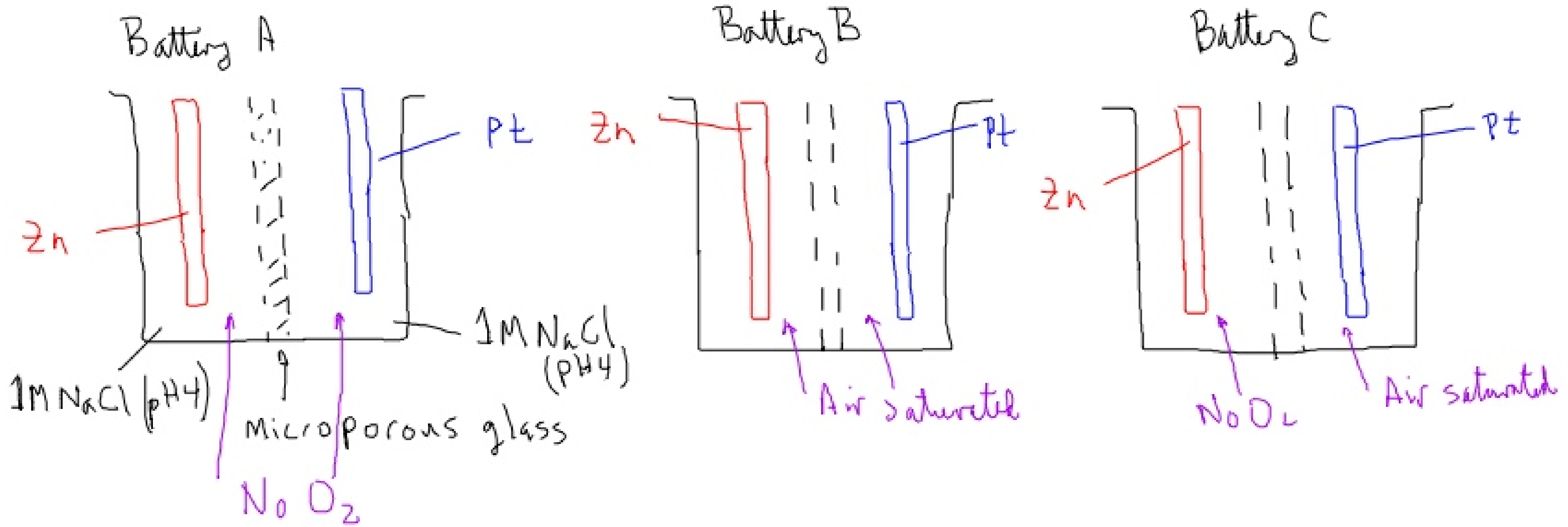
1pt. $H_2 \rightarrow 2H^+ + 2e^-$ } reaction occurring at negligible rate

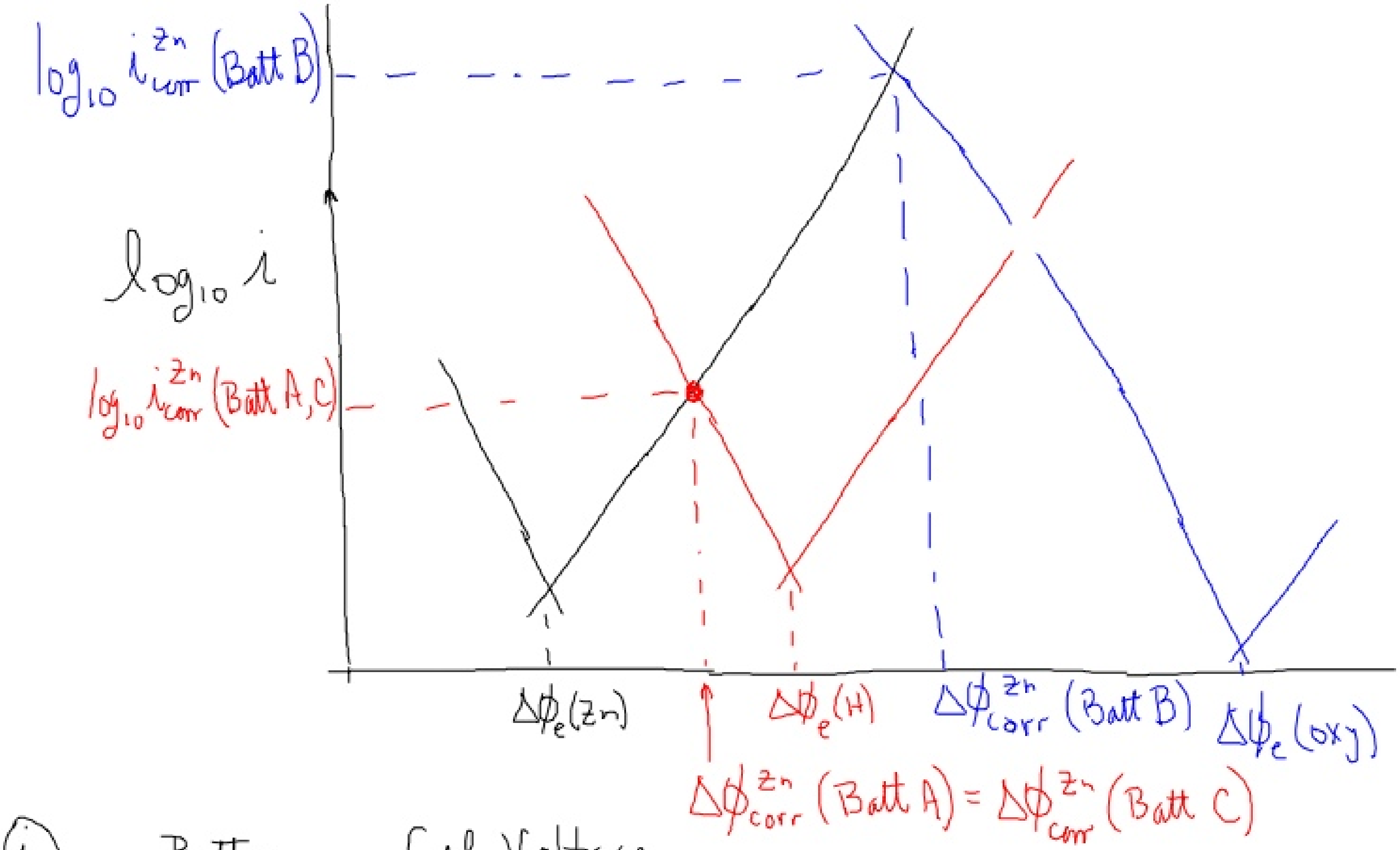
1pt. $Pt \rightarrow Pt^{++} + 2e^-$

1pt. $Pt^{++} + 2e^- \rightarrow Pt$

} negligible

(c.)





ⓘ

	Battery	Cell Voltage	
5 pts	A	$\Delta\phi_e(H) - \Delta\phi_{corr}^{Zn}(\text{Batt A})$	← Smallest Cell Voltage
5 pts	B	$\Delta\phi_e(oxy) - \Delta\phi_{corr}^{Zn}(\text{Batt B})$	
5 pts.	C	$\Delta\phi_e(oxy) - \Delta\phi_{corr}^{Zn}(\text{Batt C})$	← Largest Cell Voltage

(ii)

	Battery	i_{corr}^{Zn}	
5 pts	A	i_{corr}^{Zn} (Batt A,C)	
5 pts.	B	i_{corr}^{Zn} (Batt B)	← Shortest Shelf Life
5 pts.	C	i_{corr}^{Zn} (Batt A,C)	

Thus, Battery C is the best – it provides the highest Cell Voltage and is tied with Battery A for the longest shelf life