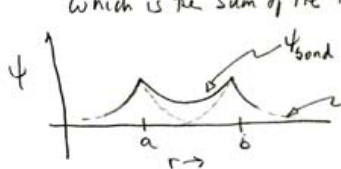# E45 MidTerm 2006 Solutions

1.

(a) Briefly explain why the energy of a hydrogen molecule, H_2, with both electrons in the bonding orbital is lower than the energy of two hydrogen atoms in which each electron is in the 1s state.

The bonding orbital's wave function is given by $\psi_a + \psi_b = \psi_{bond}$, which is the sum of the two 1s atomic orbitals from the two H nuclei: a and b.

ψ_{bond}^2 is high in the space ① between the 2 nuclei. The coulombic attraction of each e^- to the two nuclei lowers the energy as does the screening ② effect of the 2 electrons, which lowers the internuclear repulsion.

(b) Briefly explain why the energy of a hydrogen molecule, H_2, with both electrons in the anti-bonding orbital is higher than the energy of two hydrogen atoms in which each electron is in the 1s state.

The anti-bonding orbital is given by $\psi_a - \psi_b = \psi_{ANTI}$.
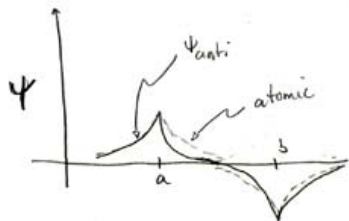
In the anti-bonding molecular orbital, the electrons have a higher probability of lying outside of the region between the 2 nuclei. As a ① result → internuclear repulsion is strong and ② coulombic attraction between one e^- and the other nucleus is weak.

(c) Briefly explain why the crystal structure of almost every metallic element is either fcc, hcp or bcc.

{ "Molecular orbitals" in a metal extend throughout the crystal.

① { The bonding is between the positively charged cores and the "sea of bonding electrons." The bond energy is lowered (as in the case of H_2)
① { by having the nuclei close and the bonding electrons between them.

Thus, want a high packing density of the cores.

① { fcc and hcp provide the highest packing density of uniform size { hard spheres. The coordination number of fcc + hcp is 12.

① { Bcc has lower packing density of identical hard spheres but the 2nd nearest { neighbor distance is only ≈ 15% greater than the nearest neighbor { distance. Consequently, the CN of bcc is often expressed
" 8 + 6 ", where 8 = # of nearest neighbors and 6 = # of 2nd nearest neighbors

(3.)

(d) Briefly explain why solid helium is not an electrical conductor but solid magnesium is.

$$He: \quad 1s^2$$

He_2 : 2e's in bonding orbital and 2e's in antibonding orbital

① Thus, thinking of solid He as He_n, where n is very large number,

① the energy band associated with the $1s$ atomic orbitals is <u>completely filled</u>. There is a large gap in energy between the $1s$-related band and the $2s$-related band. Consequently, the e's do not have access to empty states.
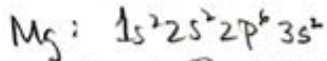
$$Mg: \quad 1s^2 2s^2 2p^6 3s^2$$

② { The energy band associated with the $3s$ atomic states is full. However, the energy band associated with $3p$ atomic states is empty and overlaps the $3s$-related band.

(e) The electronic structure of an Fe atom (Z=26) is given by $1s^2 2s^2 2p^6 3s^2 3d^6 4s^2$. The five boxes below represent the ten possible 3d states. Each box can accommodate 2 electrons. Indicate in the figure the occupied 3d states and the direction of electron spin in each of the occupied 3d levels.

② | ↓↑ | ↑ | ↑ | ↑ | ↑ |

Key: Hund's rule - want to maximize the number of parallel spins.

(4.)

2.

(a) What determines the relative values of the standard reduction potentials of elements listed in the Table on the front page of the exam booklet. (either is ok)

③

The relative tendency of element to give up (or acquire) an electron

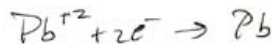(b) List four methods for lowering the corrosion of a metal in an aqueous solution.
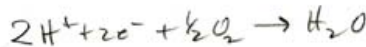
④

any combination of four

(1) Cathodic polarization (or cathodic protection)
(2) Galvanic coupling
(3) Add inhibitors to electrolyte
(4) use passive film-forming alloys
(5) High electrical resistance coatings

(c) According to the Environmental Protection Agency, the concentration of lead (Pb) in drinking water should be no greater than a few parts per billion (ppb). What concentration of Pb^{++} is required to stop the corrosion of a lead pipe that is carrying drinking water that is saturated with air and that has a pH of 8.0? (Note: 1 ppb of Pb in water is equal to 4.75×10^{-9} moles of lead per liter of water, i.e., 4.75×10^{-9}M. You may express the concentration of lead in units of ppb or M)

Corrosion will stop when the equilibrium potential of Pb equals the equilibrium potential of oxygen.

$$Pb^{+2} + 2e^- \rightarrow Pb$$

③→ $\Delta\phi_e(Pb) = -0.126 - \dfrac{.0592v}{2} \log \dfrac{(Pb)^1}{(Pb^+)}$

$$2H^+ + 2e^- + \tfrac{1}{2}O_2 \rightarrow H_2O$$

③→ $\Delta\phi = 0.829 - \dfrac{.0592}{2} \log \dfrac{(H_2O)^1}{P_{O_2}^{\frac{1}{2}}(H^+)^2}$ = 0.345V

③

Solve: $-0.126 + \dfrac{.0592}{2} \log(Pb^+) = 0.829 + \dfrac{.0592}{2}\left[\log\left(P_{O_2}^{\frac{1}{2}}\right) + \log(H^+)^2\right]$

Assume $P_{O_2} = 0.2$ $(H^+) = 10^{-8}$

$-0.126 + \dfrac{.0592}{2} \log(Pb^+) = 0.829 + \dfrac{.0592}{2}\left[-0.3495 - 14\right]$

②——→ ∴ $(Pb^+) = 10^{+9}$M = 8.2 x 10¹⁵M

→ Cannot stop oxidation of lead.

3.

When nickel is immersed in deaerated 1M HCl at 25° C, a large number of gas bubbles are formed on the surface. The corrosion potential of nickel is measured to be –0.05V vs. SHE and a steady state concentration of Ni^{++} of 10^{-5} M develops on the solution side of the interface. The exchange current density for the oxidation of nickel immersed in 1M HCl is 4.23×10^{-6} A/cm². The slope of the kinetics of the oxidation of nickel in 1M HCl is 12.5 V^{-1} (i.e., $\Delta(\log_{10}i)/\Delta(\Delta\phi) = 12.5V^{-1}$). The slope of the kinetics of the reduction reaction on nickel in oxygen-free 1M HCl is -5.55 V^{-1}.

(a) Determine the corrosion rate of nickel.

(b) Determine the exchange current density of H^+ reduction on nickel.

kinetics of $Ni \rightarrow Ni^{++} + 2e^-$

Slope = -5.55 V^{-1}

kinetics of $2H^+ + 2e^- \rightarrow H_2$

$\log i_{corr}$

$\log(4.23\times10^{-6})$

$\log[i_o(H)]$

$\Delta\phi_e(Ni) - 0.05V \qquad \Delta\phi_e(H)$
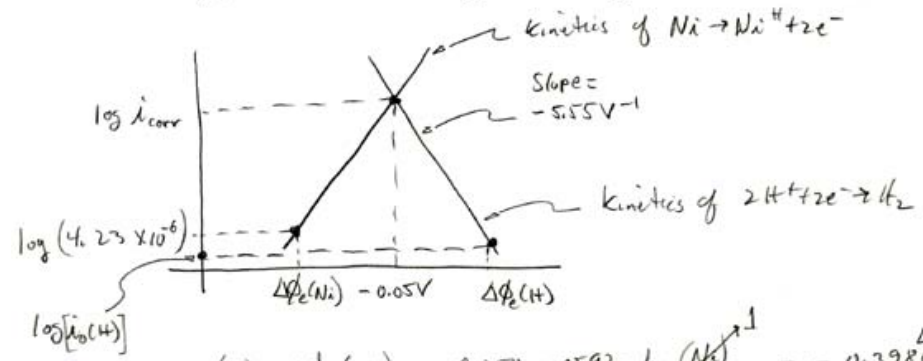
(a) $\Delta\phi_e(Ni) = -0.250 - \dfrac{.0592}{2}\log\dfrac{(Ni)}{10^{-5}} = -0.3980$

Ni Oxidation kinetics

$12.5(\Delta\phi - \Delta\phi_e) = 12.5V^{-1}[\log i - \log i_o]$

$12.5(\Delta\phi - 0.398) = 12.5[\log i - \log(4.23\times10^{-6})]$

At $\Delta\phi_{corr}$:

$12.5(-0.05 + 0.398) = 12.5[\log i_{corr} + 5.3737]$

$i_{corr} = 4.51\times10^{-6}$ A/cm²

$i_{corr} = 0.095$ A/cm²

(b) $\Delta\phi_e(H) = 0 - \dfrac{.0592}{2}\log\dfrac{P_{H_2}}{[H^+]^2} = 0$

Kinetics of H^+ reduction:

$\Delta\phi - \Delta\phi_e = -5.55[\log i - \log i_o]$

At $\Delta\phi_{corr}$:

$-0.05V - 0 = -5.55[\log(4.51\times10^{-6}) - \log i_o]$

$i_o(H) = 4.42\times10^{-6}$ A/cm²

4.

(a) What are the Miller Indices of a plane that intercepts the crystal axes at x=3, y=2, and z=1?

3

Intercepts	3	2	1
Reciprocal	$\frac{1}{3}$	$\frac{1}{2}$	1
Clear. fractions	2	3	6
M.I.		(2 3 6)	

(b) Calculate the spacing between parallel planes that have the Miller Indices determined in part (a).

3

$$d_{hke} = \frac{a}{\sqrt{h^2+k^2+\ell^2}} = \frac{a}{7}$$

(c) Specify the direction perpendicular to the plane in part (a).

3

$$[2 3 6]$$

(d) Calculate the angle between [112] and the normal to the plane in part (a).

3

$$\cos \alpha = \frac{[2 3 6]}{\sqrt{4+9+36}} \cdot \frac{[112]}{\sqrt{1+1+4}} = \frac{2+3+12}{\sqrt{294}} = 0.9915$$

$$\Rightarrow \alpha = 7.49°$$

5.

This question asks you to calculate the entropy change of the system plus surroundings for the following chemical reaction: $H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$. That is, gaseous hydrogen and oxygen react to form liquid water, which occurs spontaneously and isothermally at room temperature (298K). At 298K, the heat of the irreversible reaction at constant pressure is -68,317 cal/mole. Under reversible conditions the heat of the reaction is -11,627 cal/mole.

(a) calculate the entropy change for the system (i.e., $H_{2(g)}$, $O_{2(g)}$ and $H_2O_{(l)}$).

(b) calculate the entropy change for the surroundings (which may be thought of as a heat reservoir at temperature 298K), and show that the entropy change for the system plus surroundings for the irreversible reaction is greater than zero.

⑦

(a) $\quad \Delta S_{sys} = \dfrac{Q_{rev}}{T} = -\dfrac{11,627 \text{ cal/mole}}{298\,K} = -39.02 \dfrac{cal}{mole \cdot k}$

⑦

(b) $\quad \Delta S_{surr} = \dfrac{\text{Heat added from System}}{T} = \dfrac{+68,317 \text{ cal/mole}}{298k} = 229.25 \dfrac{cal}{mole}$

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = -39.02 + 229.25 = 190.24 \dfrac{Cal}{mole \cdot k} > 0$

④

6.
A common brass consists of 60 atomic percent (a/o) copper alloyed with 40 a/o zinc. The diffusion coefficient of zinc in copper is measured as a function of temperature and the values are listed in the table. Estimate the energy required to form vacancies in 60-40 Brass.

D (cm^2/s)	T(°C)
10.533 x 10^{-16}	700
1.0 x 10^{-16}	600

② for either eqtn
$$D = D_0 \exp^{-\frac{Q}{RT}}$$
$$\ln \frac{D}{D_0} = -\frac{Q}{RT}$$

⑩
$$\therefore \ln \frac{D_1}{D_2} = -\frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln \frac{10.533 \times 10^{-16}}{1 \times 10^{-16}} = \frac{-Q}{1.987}\left(\frac{1}{973} - \frac{1}{873}\right)$$

$$2.3545 = +Q\,(0.00059)$$

④ $Q = 39,907 \frac{cal}{mole}$