Chemistry 130A	Third Midterm Exam	Nov. 15, 1999	50 min	1 2 3 4	
Name		Discussion TA			
Prof. K. Sauer Total Points - 100	SHOW YOUR WORK			T	

Gas Constant $R = 8.314\ J\ K^{-1}\ mol^{-1} = 0.082\ L\ atm\ K^{-1}\ mol^{-1}$
Faraday constant $F = 9.6485 \times 10^4\ C\ mol^{-1} = 9.6485 \times 10^4\ J\ volt^{-1}\ mol^{-1}$
$1\ nm = 10^{-7}\ cm = 10^{-9}\ m$

Standard Reduction Potentials at 25°C		E0′ (V,pH 7)
Acetate/acetaldehyde	$OAc^- + 3H^+ + 2e^- \rightarrow CH_3CHO + H_2O$	-0.581
$H^+/H_2/Pt$	$2H^+ + 2e^- \rightarrow H_2$	-0.421
CO_2/formate	$CO_2 + 2H^+ + 2e^- \rightarrow HCO_3^- + H^+$	-0.42
$NAD^+/NADH$	$NAD^+ + H^+ + 2e^- \rightarrow NADH$	-0.320
Acetaldehyde/ethanol	$CH_3CHO + 2H^+ + 2e^- \rightarrow CH_3CH_2OH$	-0.197
Pyruvate/lactate	$CH_3COCO_2^- + 2H^+ + 2e^- \rightarrow CH_3CHOHCO_2^-$	-0.18
$O_2/H_2O_2/Pt$	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	+0.295

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1. (Credit 10+12+8)

Use the data in the table above to answer the following.

a) NAD^+ is an oxidizing agent and NADH is a reductant. Will NAD^+ more readily oxidize ethanol to acetaldehyde or acetaldehyde to acetate at pH 7? Explain your reasoning.

b) The enzyme lactate dehydrogenase catalyzes the reaction

$$CH_3CHOHCO_2^- + NAD^+ \overset{\text{lactate dehydrogenase}}{\rightleftharpoons} CH_3COCO_2^- + NADH + H^+.$$

What is the equilibrium constant for this reaction, K´ at pH 7?

c) Based on the standard cell potential, $E^{0\prime}_{cell}$ at pH 7, for the reaction in part b, calculate E'_{cell} at pH 7.5.

2. (Credit 8+8+6)

Dr. Andrew H. Smith, official physician in the 1870's to the New York and Brooklyn Bridge Co., observed that a high proportion of the 102 workers who suffered from the bends (decompression sickness) were corpulent -- over average weight. All of the deaths and 8 out of 13 paralysis cases were among obese men. At this period in the bridge construction industry the breathing mixture used in underwater caissons was pressurized air, not enriched in O_2 and not with He or other gases added.

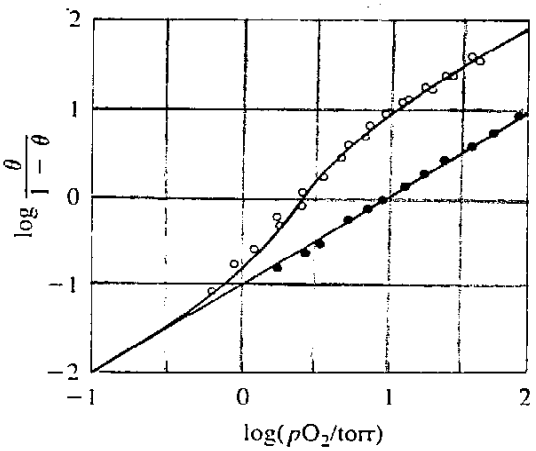
a) Propose an explanation for this observation based on your knowledge of thermodynamic principles.

b) What colligative property is most relevant to your explanation, and specifically how does it help to understand the origin of Dr. Smith's observation?

c) Apart from suggesting that the obese men should lose weight, what strategy would you suggest to the supervisors to institute immediately to decrease the incidence of bends?

3. (Credit 6+10)

Hemocyanins are respiratory proteins (O_2-binding proteins) in arthropods. For example, the hemocyanin from the spiny lobster is a protein [MW 75,000 Da] that contains Cu at the O_2-binding site. The native form of the enzyme is a hexamer, consisting of six identical subunits, each with an active binding site. In the graph are Hill plots of the binding of O_2 by spiny lobster hemocyanin as monomers (solid circles, ●) and hexamers (open circles, O).



a) What can you conclude from the Hill plots as to whether O_2-binding is cooperative, anti-cooperative or non-cooperative in monomeric hemocyanin?

hexameric hemocyanin?

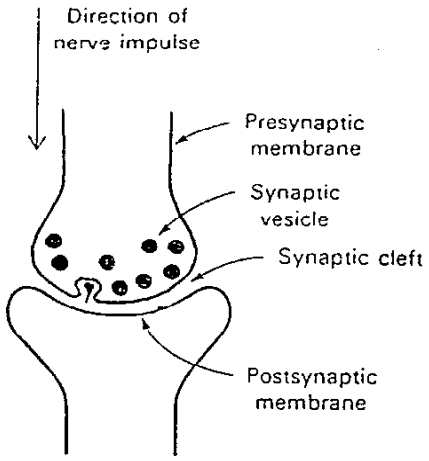
Explain your reasoning.

b) What are the values of p50 for monomeric hemocyanin?

hexameric hemocyanin?

4. (Credit 12+10)

When a sympathetic nerve fiber innervates (excites) smooth muscle, norepinephrine $(HO)_2C_6H_3CH_2CH_2\overset{+}{N}H_2CH_3$ [MW 168 Da] is the transmitter that is released at the smooth-muscle junctions. The norepinephrine must then diffuse across the synaptic cleft, approximately 50 nm, to activate the postsynaptic membrane. The diffusion constant of norepinephrine is about 0.7×10^{-5} cm^2s^{-1}.



a) How long is required for norepinephrine to transmit the signal from the presynaptic to the postsynaptic membrane?

b) If the diffusable signal transmitter was, instead, an enzyme like monoamine oxidase [MW = 120,000 Da], what difference would this make in the rate of signal transduction?