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PROBLEMS

- Sketch the structure of the following:
 - Citric acid: $\text{HOC}(\text{CH}_2\text{CO}_2\text{H})_2\text{CO}_2\text{H}$
 - Tartaric acid: $\text{HO}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2\text{H}$ (2,3,-dihydroxybutanedioic acid).
- Write the chemical formula and sketch the structure of 2-hydroxy-propanoic acid (lactic acid).
- Suppose you could follow the pathway of individual atoms during photosynthesis. While this is not possible, something similar can be done by isotopic labelling of water and CO_2 . If ^{18}O -labelled water is added to a suspension of photosynthesizing chloroplasts, which of the following compounds will first show enrichment in ^{18}O : ATP, NADPH, O_2 , or 3-phosphoglycerate? If you repeat the experiment with ^2H -labelled water and ^{13}C -labelled CO_2 , which of these molecules will first show enrichment in these isotopes?
- The first and second acidity constants of oxalic acid ($(\text{COOH})_2$) are $\text{pK}_{\text{a}1} = 1.23$ and $\text{pK}_{\text{a}2} = 4.19$. What is the pH of a solution formed by dissolving 1 mole of oxalic acid in 1 kg of water?
- If the 1 M oxalic acid solution of Problem 4 is titrated with 1 M NaOH, how will pH change as a function of the amount of base added? Make a plot of pH versus amount of base added.
- The rate of bond cleavage during the thermal maturation of kerogen approximately doubles for every 10°C rise in temperature. Thermal maturation reaches a peak at $\sim 100^\circ\text{C}$. Based on this and assuming that these reaction rates show an Arrhenius temperature dependence (equation 5.22), estimate the activation energy for these reactions.
- Astrophysicist Thomas Gold suggested that most petroleum deposits are formed by abiogenic organic carbon (mainly in the form of methane) diffusing out of the mantle. There are few, if any, geochemists that agree. Describe at least three *geochemical* observations that support the “conventional” theory that petroleum is formed from sedimentary kerogen, which in turn is derived from the remains of once-living organisms.
- Bartschat *et al.* (1992) modeled the metal-complexing behavior of humic acid as that of two ligands: a bidentate carboxylic ligand (e.g., malonate) and a bidentate phenol one (e.g., catechol), and that the effective concentrations of these are 10^{-3} mol/g humate and 5×10^{-4} mol/g humate respectively. Using the following apparent stability constants, calculate the fraction of copper complexed if the humate concentration is 10 mg/l, the pH 8, and the total copper concentration is 10^{-8} M. Assume that copper and humate are the only species present.

Apparent stability constants:

“Malonate”:	H_2L	$\beta_2 = 8.7$
	HL	$\beta_1 = 5.7$
	CuL	$\beta_{\text{Cu}} = 5.7$
“Catechol”:	H_2L	$\beta_2 = 9.1$
	HL	$\beta_1 = 12.4$
	CuL	$\beta_{\text{Cu}} = 13.4$

9. Repeat the calculation in Problem 8, but for pH 5.5.

	K_{OW}	K_{OM}
Acetophenone	38.90	42.66
Benzene	128.82	83.18
Tetrachloroethylene	398.11	208.93
Napthalene	2290.87	1288.25
Parathion	6456.54	1148.15
Pyrene	151356.12	83176.38
Chlorobenzene	512.86	389.05
DDT	1548816.62	138038.43
2,4,5,2',4',5'-PCB	5248074.60	218776.16

10. The above table lists organic solid/water (K_{OM}) and octanol/water (K_{OC}) partition coefficients for some non-polar compounds. Are these data consistent with eqn 12.15? What values do you determine for constants a and b ? (*HINT*: Use linear regression.)
11. Sediment from a highly eutropic lake was found to have an organic carbon fraction of 5.8%. Using the adsorption partition coefficient for DDT listed in Problem 10, predict the concentration of DDT in the sediment if the lake water has a DDT concentration of $3\text{ }\mu\text{g/l}$ and the sediment contains 5.8% organic matter.

Appendix

PHYSICAL AND CHEMICAL CONSTANTS

Speed of light (c)	$2.998 \times 10^8 \text{ m/s}$
Planck's Constant (h)	$6.626 \times 10^{-34} \text{ J/Hz}$
Boltzmann's Constant (k)	$1.380 \times 10^{-23} \text{ J/K}$
Gravitational constant (G)	$6.672 \times 10^{-11} \text{ N-m}^2/\text{kg}$
Avagadro's Number (N_A)	$6.022 \times 10^{23} \text{ mol}^{-1}$
Gas constant (R)	8.314 J/mol-K (1.987 cal/mol-K)
Electron charge (e)	$1.602 \times 10^{-19} \text{ coulombs (C)}$
Faraday Constant (F)	$96.485 \text{ C/mole} = \text{kJ/V-eq.}$
Permittivity in vacuum (ϵ)	$8.85 \times 10^{-12} \text{ C}^2/\text{J-m}$
Dielectric constant of water	78.54

THE EARTH

Mass of the Earth (M_\oplus)	$5.97 \times 10^{24} \text{ kg}$
Mantle	$4.0 \times 10^{24} \text{ kg}$
Core	$1.94 \times 10^{24} \text{ kg}$
Continental Crust	$2.2 \times 10^{22} \text{ kg}$
Oceans	$1.4 \times 10^{21} \text{ kg}$
Atmosphere	$5.1 \times 10^{18} \text{ kg}$
Mean radius	$6.37 \times 10^6 \text{ m}$
Radius of core	$3.47 \times 10^6 \text{ m}$
Radius of orbit	$1.49 \times 10^{11} \text{ m}$

THE SUN

Mass	$1.99 \times 10^{30} \text{ kg}$
Radius	$6.96 \times 10^8 \text{ m}$

SI UNITS AND CONVERSIONS

In the SI system, fundamental units are the kilogram, meter, and second. Consequently, preferred units of volume, pressure, and energy are m^3 , pascals, and joules, respectively.

Mass	Kilogram (kg)
Pound	1 lb = 0.4535 kg (1 kg = 2.205 lb)
u (unified atomic mass unit; also Dalton (Da))	1 u \equiv one twelfth mass of ^{12}C atom 1 u = 1.66×10^{-27} kg 1 u = 931.49 MeV/c ²
Distance	Meter (m)
inch	1 in = 0.0254 m
ångstrom	1 Å $\equiv 10^{-10}$ m
mile (US)	1 mi = 1609 m
astronomical unit (AU)	1 AU $\equiv 1.49 \times 10^{11}$ m
parsec	1 parsec = 3.084×10^{16} m = 2.07×10^5 AU
light-year	= 3.26 ly 1 ly = 6.35×10^4 AU
Force	Newton (N)
	1 N $\equiv 1$ kg-m/s ²
	1 dyne = 10^5 N
	1 dyne $\equiv 1$ gm-cm/sec ²
Energy	Joule (J)
erg	1 J $\equiv 1$ kg-m ² /s ² 1 erg = 10^{-7} J
calorie	1 erg = 1 gm-cm ² /sec ² 1 calorie = 4.184 J
liter-atmosphere	1 l-atm = 101.29 J
liter-Pascal	1 l-Pa = 99.98×10^{-5} J
electron-volt	1 eV = 1.602×10^{-19} J
u (Dalton)	1 u = 9.315×10^2 MeV
volt	1 volt-coloumb = 1 J
kilowatt-hour	1 kWh = 3.6×10^6 J
Pressure	Pascal (Pa)
pascal	1 Pa $\equiv 1$ N/m ² = 1 kg/m-s ²
bar	1 bar = 10^5 Pa (= 0.1 MPa)
atmosphere	1 atm = 1.013×10^5 Pa
Volume	Liter (l)
	1 l $\equiv 10^3$ cm ³
	1 l = 10^{-6} m ³
US gallon	1 gal = 3.785 l
Concentration	moles/l (M)
molarity	moles/kg (m)
molality	1 μM (micromole) = 10^{-6} M 1 nM (nanomole) = 10^{-9} M 1 pM (picomole) = 10^{-12} M 1 fM (femtomole) = 10^{-15} M
Radioactivity	Becquerel (Bq)
curie (Ci)	1 Bq \equiv 1 decay per second 3.7×10^{10} Bq (1 curie is the activity of 1 g of ^{226}Ra)

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