Chemistry 4A, Exam I
September 10, 1999
Professor R.J. Saykally

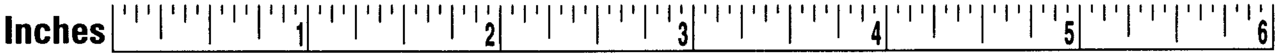
Name ____ __________

TA ____ __________

1. (20) 20
2. (20) 6+ 7=13
3. (40) 14
4. (10) 1
5. (10) 5

TOTAL EXAM SCORE (100) 53

Rules:
- Work all problems to 2 significant figures
- No lecture notes or books permitted
- No word processing calculators
- Time: 50 minutes
- Show all work to get partial credit
- Periodic Table, Tables of Physical Constants, Conversion Factors included



Periodic Table of the Elements

Atomic number → 27
Atomic mass → 58.93
Co ← symbol:
Cobalt ← name

Black naturally occurring
White synthetically prepared
most stable isotope

▨ **Metals**
■ **Metalloids**
▩ **Nonmetals**
☐ **Noble gases**

H																	2 4.003 **He** Helium
3 6.94 **Li** Lithium	4 9.01 **Be** Beryllium											[illegible]	C	N	O	F	10 20.18 **Ne** Neon
11 22.99 **Na** Sodium	12 24.31 **Mg** Magnesium											13 26.98 **Al** Aluminum	[illegible]	P	S	Cl	18 39.95 **Ar** Argon
19 39.10 **K** Potassium	20 40.08 **Ca** Calcium	21 44.96 **Sc** Scandium	22 47.90 **Ti** Titanium	23 50.94 **V** Vanadium	24 51.996 **Cr** Chromium	25 54.94 **Mn** Manganese	26 55.85 **Fe** Iron	27 58.93 **Co** Cobalt	28 58.70 **Ni** Nickel	29 63.55 **Cu** Copper	30 65.37 **Zn** Zinc	31 69.72 **Ga** Gallium	Ge	As	**Se**	**Br**	36 83.80 **Kr** Krypton
37 85.47 **Rb** Rubidium	38 87.62 **Sr** Strontium	39 88.91 **Y** Yttrium	40 91.22 **Zr** Zirconium	41 92.91 **Nb** Niobium	42 95.94 **Mo** Molybdenum	43 (98) Tc Technetium	44 101.07 **Ru** Ruthenium	45 102.91 **Rh** Rhodium	46 106.40 **Pd** Palladium	47 107.87 **Ag** Silver	48 112.41 **Cd** Cadmium	49 114.82 **In** Indium	50 118.69 **Sn** Tin	Sb	Te	I	54 131.30 **Xe** Xenon
55 132.91 **Cs** Cesium	56 137.33 **Ba** Barium	57 138.91 **La** Lanthanum	72 178.49 **Hf** Hafnium	73 180.95 **Ta** Tantalum	74 183.85 **W** Tungsten	75 186.21 **Re** Rhenium	76 190.20 **Os** Osmium	77 192.22 **Ir** Iridium	78 195.09 **Pt** Platinum	79 196.97 **Au** Gold	80 200.59 **Hg** Mercury	81 204.37 **Tl** Thallium	82 207.19 **Pb** Lead	83 208.98 **Bi** Bismuth	Po	At	86 (222) **Rn** Radon
87 (223) **Fr** Francium	88 226.03 **Ra** Radium	89 227.03 **Ac** Actinium	104 (261) Rf Rutherfordium	105 (262) Ha Hahnium	106 (266) Sg Seaborgium	107 (262) Ns Nielsbohrium	108 (265) Hs Hassium	109 (266) Mt Meitnerium	110 (271)	111 (272)	112 (277)	(113)	(114)	(115)	(116)	(117)	(118)

Lanthanide series ▸	58 140.12 **Ce** Cerium	59 140.91 **Pr** Praseodymium	60 144.24 **Nd** Neodymium	61 (145) Pm Promethium	62 150.40 **Sm** Samarium	63 151.96 **Eu** Europium	64 157.25 **Gd** Gadolinium	65 158.93 **Tb** Terbium	66 162.50 **Dy** Dysprosium	67 164.93 **Ho** Holmium	68 167.26 **Er** Erbium	69 168.93 **Tm** Thulium	70 173.04 **Yb** Ytterbium	71 174.97 **Lu** Lutetium
Actinide series ▸▸	90 232.04 **Th** Thorium	91 231.04 **Pa** Protactinium	92 238.03 **U** Uranium	93 237.05 Np Neptunium	94 (244) Pu Plutonium	95 (243) Am Americium	96 (247) Cm Curium	97 (247) Bk Berkelium	98 (251) Cf Californium	99 (252) Es Einsteinium	100 (257) Fm Fermium	101 (260) Md Mendelevium	102 (259) No Nobelium	103 (262) Lr Lawrencium

Note: Atomic masses shown here are the 1983 IUPAC values (maximum of six significant figures).

Physical Constants

Standard acceleration of terrestrial gravity	$g = 9.80665\ \mathrm{m\ s^{-2}}$ (exactly)
Avogadro's number	$N_0 = 6.022137 \times 10^{23}$
Bohr radius	$a_0 = 0.52917725\ \text{Å} = 5.2917725 \times 10^{-11}\ \mathrm{m}$
Boltzmann's constant	$k_B = 1.38066 \times 10^{-23}\ \mathrm{J\ K^{-1}}$
Electron charge	$e = 1.6021773 \times 10^{-19}\ \mathrm{C}$
Faraday constant	$\mathcal{F} = 96{,}485.31\ \mathrm{C\ mol^{-1}}$
Masses of fundamental particles:	
Electron	$m_e = 9.109390 \times 10^{-31}\ \mathrm{kg}$
Proton	$m_p = 1.672623 \times 10^{-27}\ \mathrm{kg}$
Neutron	$m_n = 1.674929 \times 10^{-27}\ \mathrm{kg}$
Ratio of proton mass to electron mass	$m_p/m_e = 1836.15270$
Permittivity of vacuum	$\epsilon_0 = 8.8541878 \times 10^{-12}\ \mathrm{C^2\ J^{-1}\ m^{-1}}$
Planck's constant	$h = 6.626076 \times 10^{-34}\ \mathrm{J\ s}$
Speed of light in a vacuum	$c = 2.99792458 \times 10^8\ \mathrm{m\ s^{-1}}$ (exactly)
Universal gas constant	$R = 8.31451\ \mathrm{J\ mol^{-1}\ K^{-1}}$ $= 0.0820578\ \mathrm{L\ atm\ mol^{-1}\ K^{-1}}$

Values are taken from "Quantities, Units and Symbols in Physical Chemistry," International Union of Pure and Applied Chemistry, Blackwell Scientific Publications, 1988.

Conversion Factors

Standard atmosphere	$1\ \mathrm{atm} = 1.01325 \times 10^5\ \mathrm{Pa} = 1.01325 \times 10^5\ \mathrm{kg\ m^{-1}\ s^{-2}}$ (exactly)
Atomic mass unit	$1\ \mathrm{u} = 1.660540 \times 10^{-27}\ \mathrm{kg}$ $1\ \mathrm{u} = 1.492419 \times 10^{-10}\ \mathrm{J} = 931.4943\ \mathrm{MeV}$ (energy equivalent from $E = mc^2$)
Calorie	$1\ \mathrm{cal} = 4.184\ \mathrm{J}$ (exactly)
Electron volt	$1\ \mathrm{eV} = 1.6021773 \times 10^{-19}\ \mathrm{J} = 96.48531\ \mathrm{kJ\ mol^{-1}}$
Foot	1 ft = 12 in = 0.3048 m (exactly)
Gallon (U.S.)	1 gallon = 4 quarts = 3.78541 L (exactly)
Liter-atmosphere	1 L atm = 101.325 J (exactly)
Metric ton	1 metric ton = 1000 kg (exactly)
Pound	1 lb = 16 oz = 0.45359237 kg (exactly)

1. (10+10 points)

A) Calculate the solubility of Ag_2CrO_4 (Ksp = 1.9 x 10^{-12}, MW = 331.7) in water at 25° C in units of grams/liter.

$K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$

$1.9 \times 10^{-12} = (2x)^2 (x)$

$1.9 \times 10^{-12} = x^3$

$x = 7.8_0 \times 10^{-5} \frac{mol}{L} \times \frac{331.7 g}{mol} = .026 \frac{g}{L}$

$2.6 \times 10^{-2} \frac{g}{L}$

✓

B) How many grams of Ag_2CrO_4 will dissolve in a solution that is 0.1 M in K_2CrO_4?

$K_2CrO_4 \rightarrow 2K^+ + CrO_4^{2-}$

$.1 M = [CrO_4]_0$

$K_{sp} = 1.9 \times 10^{-12} = [Ag^+]^2 [CrO_4^{2-}]$

$= (2x)^2 (.1 + x)$

assume $x \ll .1$

$x = 2.1_8 \times 10^{-6} \frac{mol}{L} = [Ag_2CrO_4]$ dissolve

assumption justified

$2.1_8 \times 10^{-6} \frac{mol}{L} \times \frac{331.7 g}{mol}$

$= 7.2 \times 10^{-4} \frac{g}{L}$

✓

2. (5 points each) Estimate (1 significant figure) the pH of the following solutions: (for H_2CO_3, $pK_1 = 6.37$, $pK_2 = 10.32$).

A) Baking Soda ($NaHCO_3$) → total dissociation ⇌ $Na^+ + HCO_3^-$

$4.2_7 \times 10^{-7} = K_a = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]}$

$HCO_3^- \rightleftharpoons H_3O^+ + CO_3^{2-}$

$-x \quad +x \quad +x$

pH = 6.4

1

B) Water in a limestone ($CaCO_3$) quarry

pH = $K_{a_2} = 4.8 \times 10^{-11}$

$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

pH = 10.3

2

C) The best buffer you can make from baking soda and baking powder (Na_2CO_3)

$HCO_3^- + CO_3^{2-}$

Best buffer: $[HCO_3^-] = [CO_3^{2-}]$

$pH = pK_{a_2} - \log \frac{[HCO_3^-]}{[CO_3^{2-}]}$

$pH = pK_{a_2} = 10.3$

✓

5

D) How many significant figures are there in pK_1 given above for carbonic acid?

Two $6.\underline{37}$--

5

3. (10 points each) Phosphoric acid ionizes in three stages in aqueous solution:

$H_3PO_4(aq) + H_2O(\ell) \leftrightarrow H_3O^+(aq) + H_2PO_4^-(aq)$
$K_{a1} = 7.5 \times 10^{-3}$

$H_2PO_4^-(aq) + H_2O(\ell) \leftrightarrow H_3O^+(aq) + HPO_4^{2-}(aq)$
$K_{a2} = 6.2 \times 10^{-8}$

$HPO_4^{2-}(aq) + H_2O(\ell) \leftrightarrow H_3O^+(aq) + PO_4^{3-}(aq)$
$K_{a3} = 2.2 \times 10^{-13}$

For titration of 100 ml of a 0.10 M solution of phosphoric acid with 0.100 <u>M</u> NaOH, calculate the pH at the following volumes of base added (converge answers to 10%): State and check all approximations.

A) 0 ml

$.100\,L \times .10\,M = \frac{.0100\text{ mol } H_3PO_4}{.100\,L} = .10\,M$

0 base

Assumptions check

⑥

$H_2O_{(\ell)} + H_3PO_4 \rightleftharpoons H_2PO_4^- + H_3O^+$

$.10\,M \quad 0 \quad 0$

$-x \quad +x \quad +x$

$K_a = 7.5 \times 10^{-3} = \frac{x \cdot x}{.10 - x}$

$0 = x^2 + 7.5 \times 10^{-3} x - 7.5 \times 10^{-4}$

$x = \frac{-7.5 \times 10^{-3} \pm \sqrt{5.6 \times 10^{-5} + .003}}{2}$

$[H_3O^+] = x = 2.4 \times 10^{-2}\,M$

$pH = -\log(2.4 \times 10^{-2}\,M) = 1.62$

B) 100 ml

②

$.0100\text{ mol } H_3PO_4$

$.100\,L \times .100\,M = .0100\text{ mol } OH^- \rightarrow 0\ H_3PO_4$

$K_{a2} = 6.2 \times 10^{-8} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]}$

$[H_3O^+] = \sqrt{K_{a_1} \cdot K_{a_2}}$

$pH = \frac{1}{2}(pk_1 + pk_2)$ K_{b3}

~~$6.2 \times 10^{-8} = \frac{x \cdot x}{\left(\frac{.0100\text{ mol}}{.200\,L} - x\right)}$~~

assume $x \ll .050\,M$

$5.6 \times 10^{-5}\,M = x$

$pH = 4.25$

check: $6.2 \times 10^{-8} = \frac{x^2}{.05}$; $5.6 \times 10^{-5}\,M$

$5.6 \times 10^{-5} = x$

①

C) 250 ml

H_3PO_4 & $H_2PO_4^-$ are neutralized

.0100 mol HPO_4^{2-}

.0500 × .100 M OH^- = .0050 mol OH^-

neutralization .0050 mol HPO_4^{2-}

BUFFER PROBLEM!

$2.2\times10^{-13} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]}$

$2.2\times10^{-13} = \frac{x\,y\left(\frac{.0050\,mol}{.350\,L}\right)}{-x}$

assume $x <$ .014 M

pH 7.26

$5.5\times10^{-8}_M = y = [H_3O^+]$

⑤

D) 300 ml

all acid neutralized ✓

check: $2.2\times10^{-13} = \frac{x^2}{(.014-5.5\times10^{-8})}$

$x = 5.5\times10^{-8}$ yes

$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$

$\frac{.0100\,mol}{.400\,L}$ 0 0

$-x$ $+x$ $+x$

$K_b = \frac{K_w}{K_{a3}} = .045 = \frac{[HPO_4^{2-}][OH^-]}{[PO_4^{3-}]}$ ✓

$.045 = \frac{x \cdot x}{.025 - x}$ ✓

NO ASSUMPTIONS

$0 = x^2 + .045x - .0011$

$x = \frac{-.045 \pm \sqrt{.0020 + .0044}}{2}$ ×5

$x = .0175\,M = [OH^-]$

pOH = .74

pH = 14.00 − .74

= 13.26 ✗

4. (5+5 points) Write the charge balance and phosphate mass balance equations for case B in Problem 3.

$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$

Charge (before neutralization) after →

$[Na^+] + [H_3O^+] = [H_2PO_4^-] + $ ~~$[HPO_4^{2-}]$~~ $+ [OH^-]$ $+ 2\,HPO_4^{2-} + 3\,PO_4^{3-}$

−4

Mass ~~$[NaOH] + [H_3PO_4]_0 = [H_2PO_4^-] + [OH^-] + [Na^+] + [H_3O^+]$~~

$2H_2O$ (not included)

−5

①

5. (10 points) A large piece of dry ice is put into a beaker of water. The pH drops to 4.00. Calculate the associated partial pressure of CO_2 (Henry's Law constant $K_{CO2} = 1.8 \times 10^3$ atm).

K_{a1} (H_2CO_3) = 4.3 x10^{-7}

K_{a2} (H_2CO_3) = 4.8 x10^{-11}

+1

$P_{CO_2} = K_{CO_2}$ [illegible] K_{CO_2}

+1

pH = 4.00 $[H_3O^+] = 1.0 \times 10^{-4}$ M

+1

$K_{a_1} = 4.3 \times 10^{-7} = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]}$

$4.3 \times 10^{-7} = \frac{[HCO_3^-]}{[H_2CO_3]} \cdot 1.0 \times 10^{-4}$

$4.3 \times 10^{-3} = \frac{[HCO_3^-]}{[H_2CO_3]}$

$233 = \frac{[H_2CO_3]}{[HCO_3^-]} \rightarrow = C_{HCO_3^-}\, x$

↓ ok ✓

$K_{a_2} = 4.8 \times 10^{-11} = \frac{[CO_3^{2-}]\, 1.0 \times 10^{-4}}{[HCO_3^-]}$

$4.8 \times 10^{-7} = \frac{[CO_3^{2-}]}{[HCO_3^-]}$

$P_{CO_2} = .023 \times 1.8 \times 10^3$ atm

~~$= 4.[illegible] \times 10^{-5}$ atm~~

find total moles of carbonates:

if CO_2 that's converted to H_2CO_3 provides all of H_3O^+,

$\chi_{H_2CO_3} = \frac{233}{233+1+4.8 \times 10^{-7}} = 99.6\%$ $\left(\frac{[H_2CO_3]}{[H_2CO_3]+[HCO_3^-]+[CO_3^{2-}]}\right)$ $[HCO_3^-]$

$\chi_{HCO_3^-} = \frac{1}{233+1+4.8 \times 10^{-7}} = 0.427\%$

$\chi_{CO_3^{2-}} = \frac{4.8 \times 10^{-7}}{233+1+4.8 \times 10^{-7}} = 1.00 \times 10^{-15}\%$

$n_{CO_2}^{1.0 L} = .023$ mol

+1

$[CO_2] = [H_2CO_3]$

$= .023$ M

Λ since volumes are equal, so are moles

H_2CO_3	$\rightleftharpoons$ HCO_3^-	+ H_3O^+	
x	0	0	
-10^{-4} M	$+10^{-4}$ M	$+10^{-4}$ M	
$x - 10^{-4}$	10^{-4}	10^{-4}	

+1

$4.3 \times 10^{-7} = \frac{10^{-8}}{x - 10^{-4}\ M}$

ok

$4.3 \times 10^{-7} x - 4.3 \times 10^{-11} = 10^{-8}$

$x = .023$ M H_2CO_3

⑤