

# Chemistry 232, Final Exam

Instructor: Bergdahl

**Summer 2014**

Name: \_\_\_\_\_

Be prepared to show ID upon request.

**\*\*No cellular phones or calculators are allowed during the test\*\***

My laboratory instructor (TA) is (Please circle):

David Schmit

Arielle Kanner

Tim Montgomery

I do not take the 232L this summer

Before you start the exam, make sure that you have 13 problems!!

My student I.D. (red I.D.) number is:

A very Good Luck

For graders only:

Problem: #1 \_\_\_\_\_/12p

#2 \_\_\_\_\_/24p

#3 \_\_\_\_\_/27p

#4 \_\_\_\_\_/16p

#5 \_\_\_\_\_/10p

#6 \_\_\_\_\_/12p

#7 \_\_\_\_\_/16p

#8 \_\_\_\_\_/15p

#9 \_\_\_\_\_/10p

#10 \_\_\_\_\_/20p

#11 \_\_\_\_\_/25p

#12 \_\_\_\_\_/13p

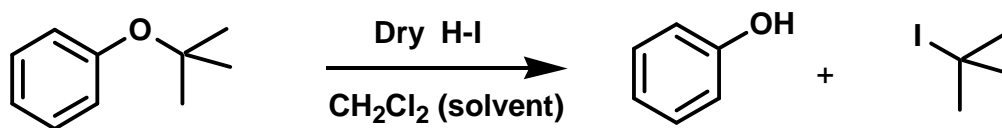
#13 \_\_\_\_\_/18p

Total: \_\_\_\_\_/218p

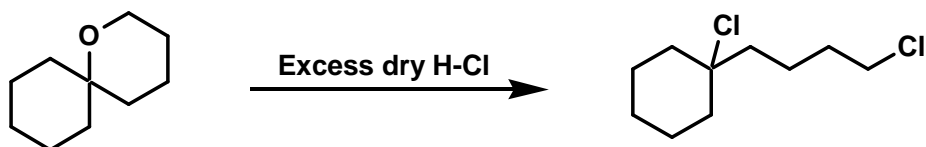
**Grand Total: \_\_\_\_\_/Max 200p**

**Problem 1.** Propose mechanisms for the following two reactions showing structures of possible intermediates and using curved arrows to indicate the electron flows in every step. (5 + 7p)

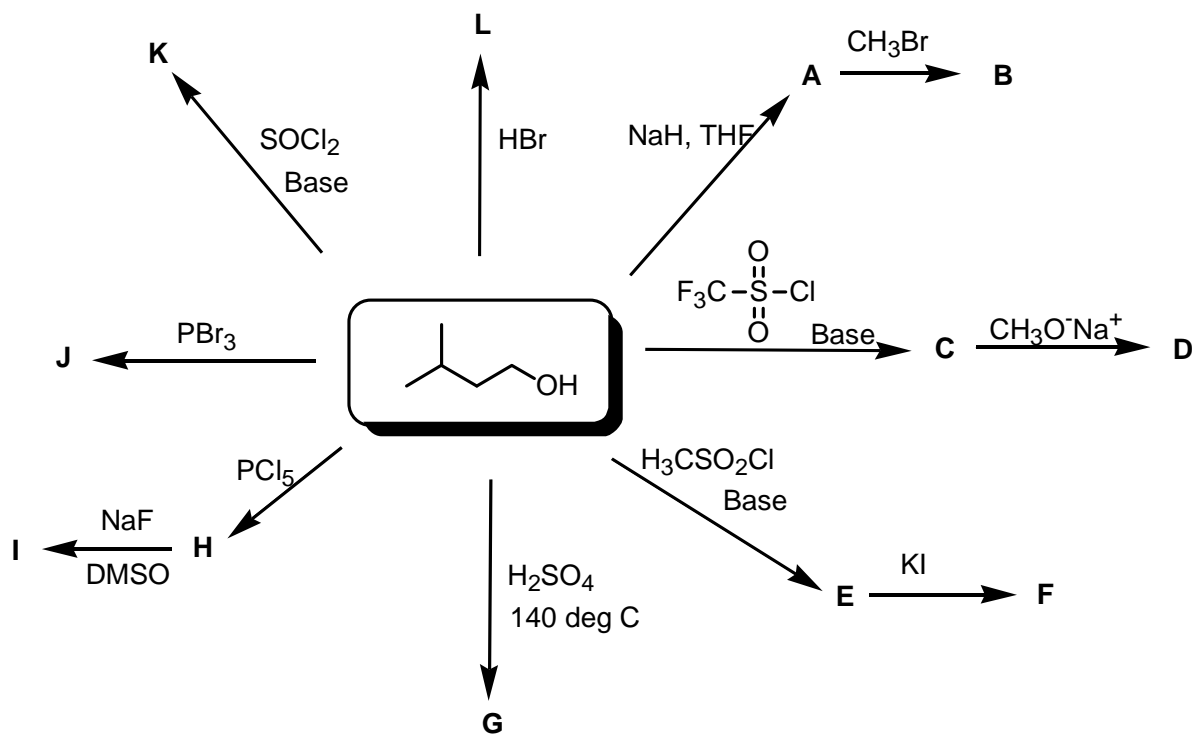
A)



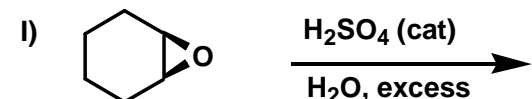
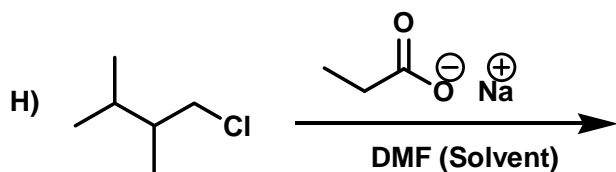
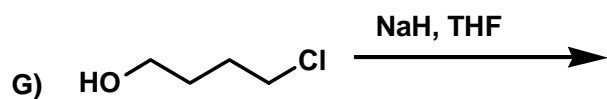
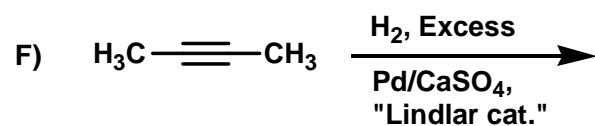
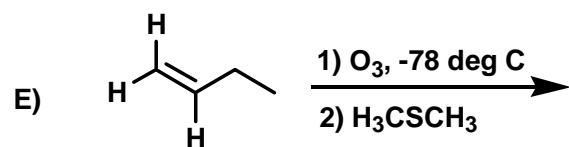
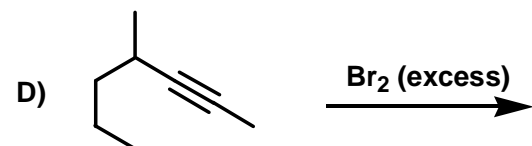
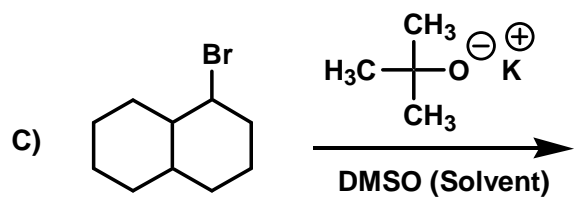
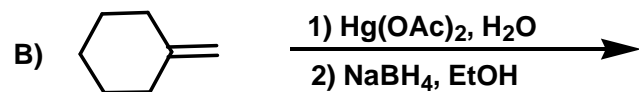
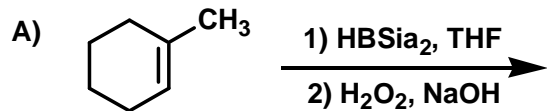
B)



**Problem 2.** Considering **A-L** to represent the major products formed in each of the following reactions. Provide a structure for each of **A** through **L**. (24p)

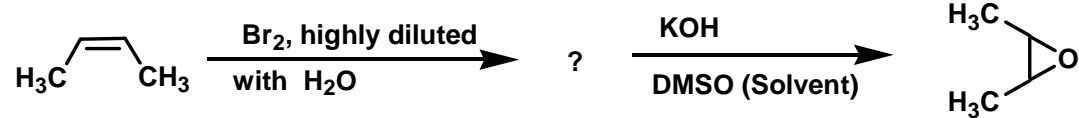


**Problem 3.** Indicate the major product formed in the following reactions. (27p)

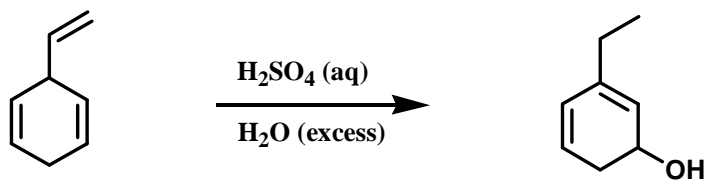


**Problem 4.** Provide detailed mechanisms for the two reactions below. (16p)

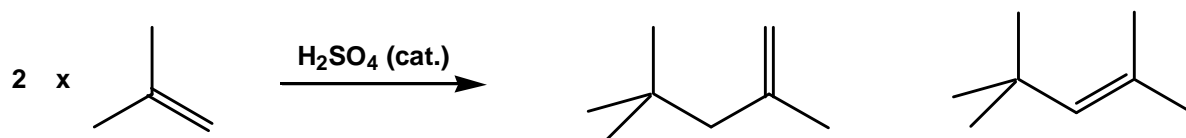
A)



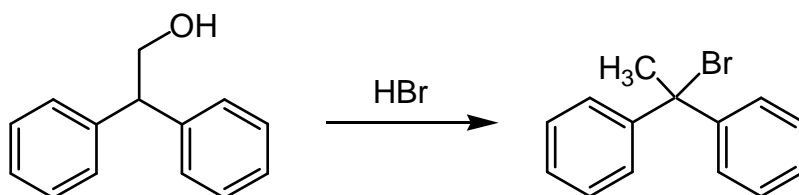
B)



**Problem 5.** Propose a mechanism that explains formation of the two products from the following reaction. (10p)

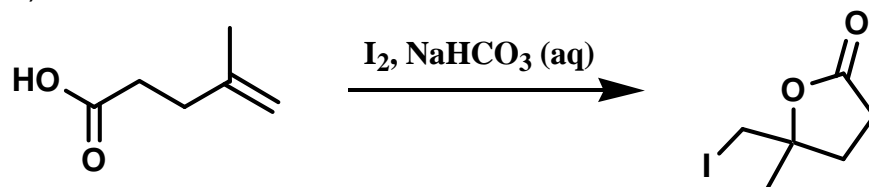


**Problem 6.** Propose a mechanism that accounts for the following reaction. (12p)

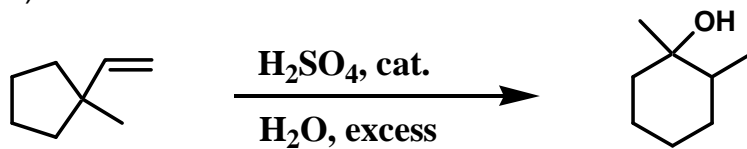


**Problem 7.** Provide reaction mechanisms for the following two reactions. (16p)

A)

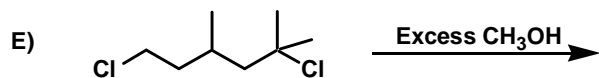
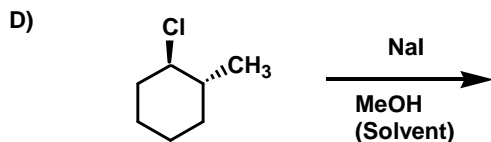
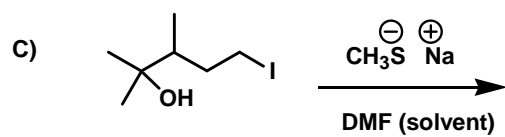
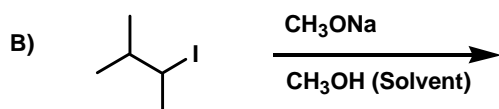
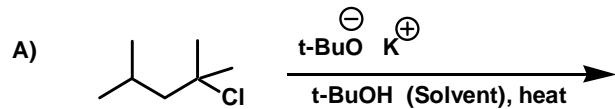


B)

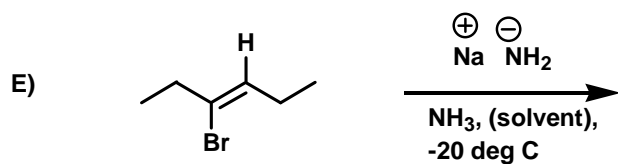
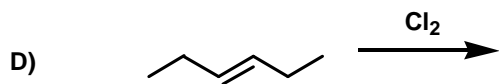
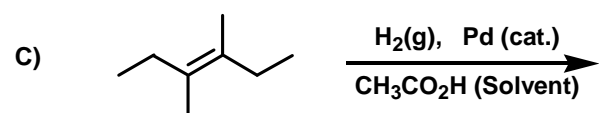
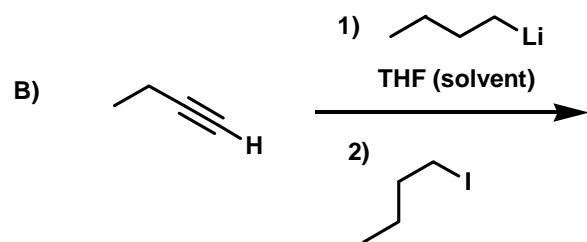
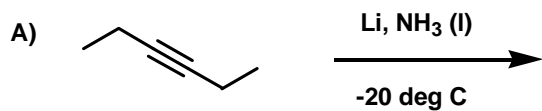




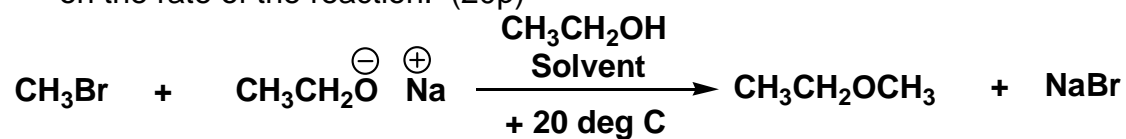
**Problem 8.** Predict the reaction pathways for the following reactions. Will it be substitution ( $S_N2$  or  $S_N1$ ) or elimination ( $E1$  or  $E2$ )? Write the structural formulas for the major organic products. (15p)



**Problem 9** Indicate the products formed in the following reactions. For full credit, correct stereochemical/constitutional isomer must be depicted (if appropriate). (10p)



**Problem 10.** Consider the reaction below. Predict and explain the effect of the changes given on the rate of the reaction. (20p)



A) Change the solvent from CH<sub>3</sub>CH<sub>2</sub>OH to DMSO.

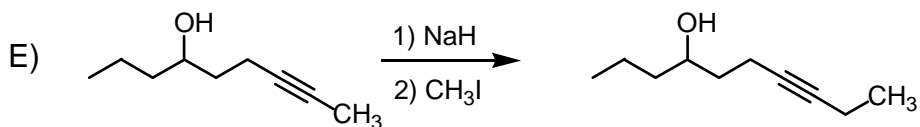
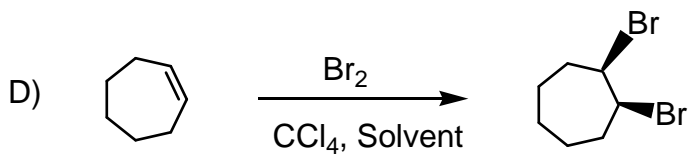
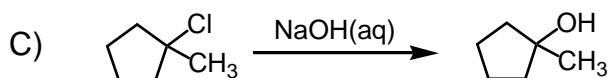
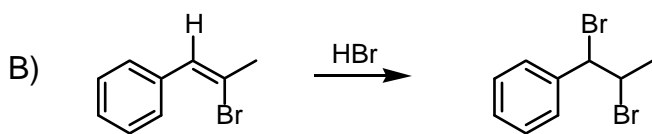
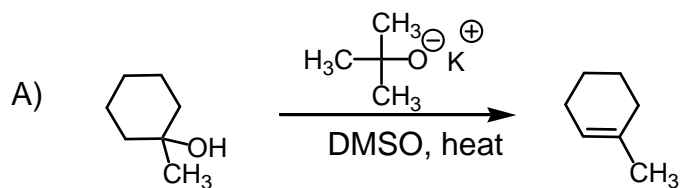
B) Change the starting material from CH<sub>3</sub>Br to CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br.

C) Change the starting material from CH<sub>3</sub>Br to CH<sub>3</sub>F.

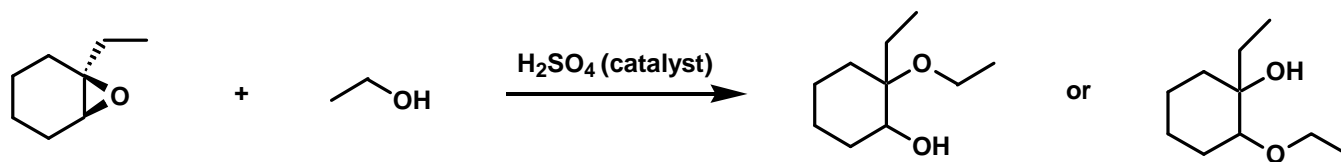
D) Change the solvent system by adding H<sub>2</sub>O to the CH<sub>3</sub>CH<sub>2</sub>OH.

E) Increase the concentration of nucleophile in the CH<sub>3</sub>CH<sub>2</sub>OH and increase at the same time the temperature from +20deg C to +40deg C.

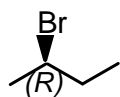
**Problem 11.** The reactions shown below are unlikely to occur as described. Tell what is wrong and predict the true product. (25p)



**Problem 12.** Predict which of these two products would form in this reaction and explain your choice showing ALL of the steps in the mechanisms. Include correct stereochemistry to the product. (13p)

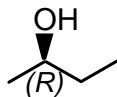


**Problem 13.** Optically active *R*-bromobutane and *R*-butanol have the optical rotations given:



(*R*)-(-)-2-Bromobutane

$$[\alpha] = - 23^\circ$$



(*R*)-(-)-2-Butanol

$$[\alpha] = - 13^\circ$$

Treatment of the bromide with NaOH in H<sub>2</sub>O yields 2-butanol with an optical rotation of  $[\alpha] = +6.5^\circ$ .

A) Is the outcome of this reaction consistent with an S<sub>N</sub>2, S<sub>N</sub>1 reaction or both? (8p)

B) What is the optical purity of the alcohol in A) after the reaction? (3p)

C) In a different flask, changing the solvent from H<sub>2</sub>O to DMSO gave  $[\alpha] = +13^\circ$  of the 2-butanol.

Is the outcome in this case consistent with an S<sub>N</sub>2, S<sub>N</sub>1 reaction or both? (5p)

What is the ratio of R/S in this case? (2p)

Scratch paper

Scratch paper



Scratch paper

# PERIODIC TABLE OF THE ELEMENTS

1 IA		2 IIA		IUPAC recommendations → Chemical Abstracts Service group notation →										13 IIIA		14 IVA		15 VA		16 VIA		17 VIIA		18 VIIIA																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																														
Atomic number →	Symbol →	Atomic number →	Symbol →	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	362	363	364	365	366	367	368	369	370	371	372	373	374	375	376	377	378	379	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439	440	441	442	443	444	445	446	447	448	449	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	484	485	486	487	488	489	490	491	492	493	494	495	496	497	498	499	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516	517	518	519	520	521	522	523	524	525	526	527	528	529	530	531	532	533	534	535	536	537	538	539	540	541	542	543	544	545	546	547	548	549	550	551	552	553	554	555	556	557	558	559	560	561	562	563	564	565	566	567	568	569	570	571	572	573	574	575	576	577	578	579	580	581	582	583	584	585	586	587	588	589	590	591	592	593	594	595	596	597	598	599	600	601	602	603	604	605	606	607	608	609	610	611	612	613	614	615	616	617	618	619	620	621	622	623	624	625	626	627	628	629	630	631	632	633	634	635	636	637	638	639	640	641	642	643	644	645	646	647	648	649	650	651	652	653	654	655	656	657	658	659	660	661	662	663	664	665	666	667	668	669	670	671	672	673	674	675	676	677	678	679	680	681	682	683	684	685	686	687	688	689	690	691	692	693	694	695	696	697	698	699	700	701	702	703	704	705	706	707	708	709	710	711	712	713	714	715	716	717	718	719	720	721	722	723	724	725	726	727	728	729	730	731	732	733	734	735	736	737	738	739	740	741	742	743	744	745	746	747	748	749	750	751	752	753	754	755	756	757	758	759	760	761	762	763	764	765	766	767	768	769	770	771	772	773	774	775	776	777	778	779	780	781	782	783	784	785	786	787	788	789	790	791	792	793	794	795	796	797	798	799	800	801	802	803	804	805	806	807	808	809	810	811	812	813	814	815	816	817	818	819	820	821	822	823	824	825	826	827	828	829	830	831	832	833	834	835	836	837	838	839	840	841	842	843	844	845	846	847	848	849	850	851	852	853	854	855	856	857	858	859	860	861	862	863	864	865	866	867	868	869	870	871	872	873	874	875	876	877	878	879	880	881	882	883	884	885	886	887	888	889	890	891	892	893	894	895	896	897	898	899	900	901	902	903	904	905	906	907	908	909	910	911	912	913	914	915	916	917	918	919	920	921	922	923	924	925	926	927	928	929	930	931	932	933	934	935	936	937	938	939	940	941	942	943	944	945	946	947	948	949	950	951	952	953	954	955	956	957	958	959	960	961	962	963	964	965	966	967	968	969	970	971	972	973	974	975	976	977	978	979	980	981	982	983	984	985	986	987	988	989	990	991	992	993	994	995	996	997	998	999	1000
1	H	2	He	3	Li	4	Be	5	Na	6	Mg	7	Al	8	Si	9	P	10	S	11	Cl	12	Ar	13	K	14	Ca	15	Sc	16	Ti	17	V	18	Cr	19	Mn	20	Fe	21	Co	22	Ni	23	Cu	24	Zn	25	Ga	26	Ge	27	As	28	Se	29	Br	30	Kr	31	Rb	32	Sr	33	Y	34	Zr	35	Nb	36	Hf	37	Ta	38	Hg	39	*La	40	Ce	41	Pr	42	Nd	43	Pm	44	Sm	45	Eu	46	Gd	47	Tb	48	Dy	49	Ho	50	Er	51	Tm	52	Yb	53	Lu	54	Cs	55	Ba	56	*Ac	57	Fr	58	Ra	59	Ac	60	Th	61	Pa	62	U	63	Np	64	Pu	65	Am	66	Cm	67	Bk	68	Cf	69	Es	70	Fm	71	Mendelevium	72	Nobelium	73	Lutetium	74	Ytterbium	75	Thulium	76	Erbium	77	Holmium	78	Terbium	79	Dysprosium	80	Neodymium	81	Europium	82	Gadolinium	83	Terbium	84	Ytterbium	85	Lutetium	86	Mercury	87	Gold	88	Silver	89	Cadmium	90	Indium	91	Tin	92	Lead	93	Bismuth	94	Polonium	95	Astatine	96	Radon	97	Francium	98	Radium	99	Actinium	100	Thorium	101	Protactinium	102	Uranium	103	Neptunium	104	Plutonium	105	Americium	106	Curium	107	Berkelium	108	Californium	109	Einsteinium	110	Fermium	111	Mendelevium	112	Nobelium	113	Lutetium	114	Ytterbium	115	Thulium	116	Erbium	117	Holmium	118	Terbium	119	Dysprosium	120	Neodymium	121	Europium	122	Gadolinium	123	Terbium	124	Ytterbium	125	Lutetium	126	Mercury	127	Gold	128	Silver	129	Cadmium	130	Indium	131	Tin	132	Lead	133	Bismuth	134	Polonium	135	Astatine	136	Radon	137	Francium	138	Radium	139	Actinium	140	Thorium	141	Protactinium	142	Uranium	143	Neptunium	144	Plutonium	145	Americium	146	Curium	147	Berkelium	148	Californium	149	Einsteinium	150	Fermium	151	Mendelevium	152	Nobelium	153	Lutetium	154	Ytterbium	155	Thulium	156	Erbium	157	Holmium	158	Terbium	159	Dysprosium	160	Neodymium	161	Europium	162	Gadolinium	163	Terbium	164	Ytterbium	165	Lutetium	166	Mercury	167	Gold	168	Silver	169	Cadmium	170	Indium	171	Tin	172	Lead	173	Bismuth	174	Polonium	175	Astatine	176	Radon	177	Francium	178	Radium	179	Actinium	180	Thorium	181	Protactinium	182	Uranium	183	Neptunium	184	Plutonium	185	Americium	186	Curium	187	Berkelium	188	Californium	189	Einsteinium	190	Fermium	191	Mendelevium	192	Nobelium	193	Lutetium	194	Ytterbium	195	Thulium	196	Erbium	197	Holmium	198	Terbium	199	Dysprosium	200	Neodymium	201	Europium	202	Gadolinium	203	Terbium	204	Ytterbium	205	Lutetium	206	Mercury	207	Gold	208	Silver	209	Cadmium	210	Indium	211	Tin	212	Lead	213	Bismuth	214	Polonium	215	Astatine	216	Radon	217	Francium	218	Radium	219	Actinium																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																	

# pKa Table (H<sub>2</sub>O Reference)

## Oxygen Acids

CF <sub>3</sub> SO <sub>2</sub> H	-14
	-12.4
	-7.8
	-6.5
	-6.2
(CH <sub>3</sub> ) <sub>2</sub> S <sup>+</sup> -H	-5.4
	-4.4
(CH <sub>3</sub> ) <sub>2</sub> O <sup>+</sup> -H	-3.8
CH <sub>3</sub> SO <sub>2</sub> -OH	-2.6
CH <sub>3</sub> OH <sub>2</sub> <sup>+</sup>	-2.2
	-2.05
(CH <sub>3</sub> ) <sub>2</sub> S=O <sup>+</sup> -H	-1.8
	-1.37
CF <sub>3</sub> CO <sub>2</sub> H	-0.25
	0.3
C <sub>6</sub> H <sub>5</sub> -CO <sub>2</sub> H	4.2
CH <sub>3</sub> -CO <sub>2</sub> H	4.76
C <sub>6</sub> F <sub>5</sub> -OH	5.5
	6.3
C <sub>6</sub> H <sub>5</sub> -SH	6.5
C <sub>6</sub> H <sub>5</sub> -OH	9.95
HCO <sub>3</sub> <sup>-</sup>	10.3
R-S-H	10.5
HO-H	15.7
CH <sub>3</sub> -OH	16
(CH <sub>3</sub> ) <sub>3</sub> C-OH	20
[t-BuOH]	

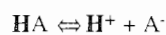
## Nitrogen Acids

+PH <sub>4</sub>	-14
C <sub>6</sub> H <sub>5</sub> -C≡N <sup>+</sup> -H	-10.5
CH <sub>3</sub> -C≡N <sup>+</sup> -H	-10
	-9.3
	-2.9
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup>	0.78
CH <sub>3</sub> -PH <sub>3</sub> <sup>+</sup>	2.7
C <sub>6</sub> H <sub>5</sub> -NH <sub>3</sub> <sup>+</sup>	4.6
	5.21
N≡C-CH <sub>2</sub> -CH <sub>2</sub> -NH <sub>3</sub> <sup>+</sup>	7.87
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> -PH <sup>+</sup>	9.1
	9.2
+NH <sub>4</sub>	9.2
CH <sub>3</sub> CH <sub>2</sub> -NH <sub>3</sub> <sup>+</sup>	10.6
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> -NH <sub>2</sub> <sup>+</sup>	11.0
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> -NH <sup>+</sup>	10.75
	13.6
C <sub>6</sub> H <sub>5</sub> -NH <sub>2</sub>	28
NH <sub>3</sub>	33

## Carbon Acids

(NO <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	3.6
	5.2
	9
N≡C-H	9.1
O <sub>2</sub> N-CH <sub>3</sub>	10.2
	10.7
(CF <sub>3</sub> ) <sub>3</sub> CH	11
(N≡C) <sub>2</sub> CH <sub>2</sub>	11.2
	13
	15
H <sub>3</sub> C-C(=O)-CH <sub>3</sub>	20
	20
	20.8
C <sub>6</sub> H <sub>5</sub> -C≡C-H	23
CH <sub>3</sub> -CO <sub>2</sub> Et	24
CH <sub>3</sub> -SO <sub>2</sub> -CH <sub>3</sub>	33
CH <sub>3</sub> -C≡N	25
H-C≡C-H	24
	29
CF <sub>3</sub> -H	32
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CH	31.5
H <sub>3</sub> C-S(=O)-CH <sub>3</sub>	33.5
C <sub>6</sub> H <sub>5</sub> -CH <sub>3</sub>	41
CH <sub>2</sub> =CH <sub>2</sub>	44
	43
	46
CH <sub>3</sub> -CH <sub>3</sub>	50

Remember that acidity is defined as follows:



Thus:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Taking the log of both sides and multiplying through by -1, we get:

$$\text{pK}_a = \text{pH} - \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Leading to this relationship, pK<sub>a</sub> is defined as -log K<sub>a</sub>; as such the more NEGATIVE the value (or the SMALLER the value) the more acidic the compound is.

All compounds shown in this Table are acids herein; the acidic H for which the pK<sub>a</sub> value is provided is indicated in bold red. All acids shown here are monoprotic; that is, only one of the bolded H's will be lost.