

# Final Exam Table; CHM 310S

## HAMMETT SUBSTITUENT CONSTANTS

Group	$\sigma_{o,p}^+$	$\sigma_{meta}$
N(CH <sub>3</sub> ) <sub>2</sub>	-1.7	-0.15
NH <sub>2</sub>	-1.3	-0.16
OH	-0.92	-0.38
OCH <sub>3</sub>	-0.78	0.11
SCH <sub>3</sub>	-0.6	0.15
C(CH <sub>3</sub> ) <sub>2</sub>	-0.26	-0.10
CH <sub>3</sub>	-0.31	-0.06
C <sub>6</sub> H <sub>5</sub>	-0.21	0.05
H	0.00	0.00
F	-0.07	0.34
Cl	0.11	0.37
Br	0.15	0.39
I	0.13	0.35
COOH	0.42	0.37
CF <sub>3</sub> <sup>*</sup>	0.54	0.43
CN	0.66	0.56
NO <sub>2</sub>	0.79	0.71

## VAPOUR PRESSURE FRAGMENTS

	$f$	$f^p$
X-C-R <sub>3</sub>	-0.38	-0.18
X-CH <sub>3</sub>	-0.28	-0.34
X-CH <sub>2</sub> -R	-0.45	-0.26
X-CH-R <sub>2</sub>	-0.39	-0.19
=CH- (in ring)		-0.46
=CX- (in ring)	-0.63	-0.63
X-F	0.07	0.21
X-Cl	-0.79	-0.53
X-Br	-1.18	-0.84
X-I	-1.71	-1.24
X-CF <sub>3</sub>	-0.20	0.32
X-CCl <sub>3</sub>	-1.89	-2.63
X-CBr <sub>3</sub>	-3.47	
X-OR	-0.43	-0.70
X-OAr	-0.70	-0.33
X-OH (primary)	-2.09	-1.79
R-OH (secondary)	-1.58	
R-OH (tertiary)	-1.52	
X-NO <sub>2</sub>	-2.51	-1.45
X-NH <sub>2</sub>	-0.80	-1.93
X-NHR	-0.86	-1.00
X-NHAr	-1.00	-1.96
X-C(=O)R	-1.63	-1.46
X-CHO	-1.21	-1.40
X-COOH	-3.67	-4.69
X-COOR	-1.43	-1.19
X-NHCOR	-4.68	-4.68
X-NHCONR <sub>2</sub>		-2.80
X-SCONR <sub>2</sub>	-3.01	
Intramolecular H-bond	0.73	0.73

## SUBSTITUENT FACTORS; F(X) AT 298 K

*OH Abstract*

X	F(X) at 298
-CH <sub>3</sub>	1.00
-CH <sub>2</sub> -, >CH-, >C<	1.23
-F	0.094
-Cl	0.38
-Br	0.28
-I	0.53
-CH <sub>2</sub> Cl, -CHCl <sub>2</sub> , -CHCl-, >CCl-	0.36
-CH <sub>2</sub> Br, CHBr-	0.46
-CCl <sub>3</sub>	0.069
-CF <sub>3</sub>	0.071
-CHF <sub>2</sub>	0.13
-CH <sub>2</sub> F	0.61
-CF <sub>2</sub> Cl	0.031
-CHF-	0.21
-CF <sub>2</sub> -	0.018
=O	8.7
-CHO, >CO	0.75
-CH <sub>2</sub> C(O), >CHC(O), >CC(O)	3.9
-C <sub>6</sub> H <sub>5</sub> , >C=C<	-1.0
-OH	3.5
-OR (R = alkyl)	8.4
-OCF <sub>3</sub> , -OCF <sub>2</sub> -, -OCHF <sub>2</sub> , -OCH <sub>2</sub> F	0.17
-C(O)Cl	0.067
-OCH <sub>2</sub> CF <sub>3</sub> , -OCH(CF <sub>3</sub> ) <sub>2</sub> , -OCHClCF <sub>3</sub>	0.44
-C(O)OR (R = alkyl)	0.31
-OC(O)F (R = alkyl)	1.6
-C(O)OH	0.74
-C(O)CF <sub>3</sub>	0.11
-ONO <sub>2</sub>	0.14
-CH <sub>2</sub> ONO <sub>2</sub> , >CHONO <sub>2</sub> , >CONO <sub>2</sub>	0.28
-CN	0.19
-CH <sub>2</sub> CN	-0.12
3-member ring	0.020
4-member ring	0.28
5-member ring	0.64
7 and 8 member ring	-1.0

Equation:  $\text{Vlog } V_p \text{ (mm Hg)} = \text{Summation } a_i f_i - 1.56(\text{mp}-25)/100 + 4.42$   
 Note: mm Hg = torr; 760 torr = 1 atm; 1 atm = 101325 Pa  
 Give your  $K_h$  values in Pa • m<sup>3</sup>/mole

## Equations

LFER for "nonpolar substituted benzenes":  
 $\log K_{ow} = -0.86 \log C_{sat} \text{ (moles/liter)} + 0.75$

OH addition to aromatic rings:

$$\log_{10} K_{add} \text{ (cm}^3 \text{ molecule}^{-1} \text{sec}^{-1}) = -11.71 - 1.34 \sum \sigma^+$$

K<sub>ow</sub> FRAGMENT CONSTANTS

	<i>f</i>	<i>f</i> <sup>Φ</sup>
-H	0.23	0.23
-C-	0.20	0.20
C aromatic	0.13	
-F	-0.38	0.37
-Cl	0.06	0.94
-Br	0.20	1.09
-I	0.59	1.35
-O-	-1.82	-0.61
-OH	-1.64	-0.44
-NO <sub>2</sub>	-1.16	-0.03
-NH-	-2.15	-1.03
Ketone -C(=O)-	-1.90	-1.09
Carboxylate -COO-	-5.19	-4.13
Carboxylic acid -COOH	-1.11	-0.03
Ester -COO-	-1.49	-0.56

Common Intramolecular Factor

Structural Feature	Symbol	Influence on K <sub>ow</sub>	F Value
--------------------	--------	------------------------------	---------

*Geometric Effects*

Unsaturation			
Double bond	F <sub>  </sub>	greater polarizability,	-0.09
Triple bond	F <sub>   </sub>	smaller size	-0.50
Skeletal arrangement			
Long-chain flexing	F <sub>ch</sub>	upsets flickering ice cavity	(n-1)(-0.12)
Ring flexing	F <sub>r</sub>	"	(n-1)(-0.09)
Nonpolar chain branch	F <sub>br nonpolar</sub>	decreases molecular size	(-0.13)
Polar chain branch	F <sub>br polar</sub>	"	(-0.22)

*Electronic Effects*

Nearby polyhalogenation	F <sub>polyhalo</sub>	Opposing nearby dipoles	
2 on same C		Diminish polarity	0.60
3 on same C			1.59
4 on same C			2.88
2 on adjacent single-bonded C			0.28
3 on adjacent single-bonded C			0.56
4 on adjacent single-bonded C			0.84
5 on adjacent single-bonded C			1.12
6 on adjacent single-bonded C			1.40
Nearby polar groups	F <sub>nearby polar groups</sub>	Opposing nearby dipoles diminish polarity	
		In Chain	In Alicyclic Ring
		In Aromatic Ring	
On same C		-0.42( <i>f</i> <sub>1</sub> + <i>f</i> <sub>2</sub> )	
On adjacent C's		-0.26( <i>f</i> <sub>1</sub> + <i>f</i> <sub>2</sub> )	-0.16( <i>f</i> <sub>1</sub> + <i>f</i> <sub>2</sub> )
On C's separated by one C		-0.10( <i>f</i> <sub>1</sub> + <i>f</i> <sub>2</sub> )	-0.08( <i>f</i> <sub>1</sub> + <i>f</i> <sub>2</sub> )
Intramolecular hydrogen bonding			
With OH	F <sub>H-bond with oxy.</sub>	Ties up moiety diminishing hydrogen bonding with water	+1.0
With NH	F <sub>H-bond with nit.</sub>		+0.6