DATA SHEET FOR CHEM 331

Universal Constants:

$R = 8.314\ J\ mol^{-1}\ K^{-1} = 0.08206\ L\ atm\ mol^{-1}\ K^{-1}$
$F = 96{,}480\ C\ mol$
$h = 6.626 \times 10^{-34}\ J\ s$
$c = 3.00 \times 10^{8}\ m\ s^{-1}$
$\kappa = 1.38 \times 10^{-23}\ m^2\ kg\ s^{-2}\ K^{-1}$

Conversions:

$1\,ppm = \frac{1\,mg}{kg} = \frac{1\,\mu g}{g} = \frac{1\,ng}{mg}$ $\qquad$ $1\,ppb = \frac{1\,\mu g}{kg} = \frac{1\,ng}{g}$

Kelvin Temperature = 273.2 + ^oC

1.00 atm = 101,300 Pa = 760 torr

$1\ m^3 = 10^3\ L$

$N_A = 6.023 \times 10^{23}\ molecule\ mol^{-1}$

$1\ J = kg\ m^2/s^2 = N\ m = Pa\ m^3 = W\ s = C\ V$

$$\chi_i = \frac{M_i}{\overline{V}_{solv}}$$

Formulas:

Rate = $-k\,[A]^n$ $\qquad$ $k = Ae^{-Ea/RT}$

$k = \left(\frac{\kappa T}{h}\right) e^{\frac{\Delta S^{\mp}}{R}} e^{\frac{-\Delta H^{\mp}}{RT}}$ $\qquad$ $\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$\ln[A] = -kt + \ln[A]_o$ $\qquad$ $\frac{1}{[A]} = kt + \frac{1}{[A]_o}$

$\Delta G = \Delta H - T\Delta S$ $\qquad$ $\Delta G^o = -RT \ln K$

$pH = -\log a_{H^+} \approx -\log [H^+]$ $\qquad$ $pH + pOH = pK_w$

Temp (^oC)	0	5	10	15	20	25
pK_w	14.94	14.73	14.53	14.35	14.17	14.00

$$\ln P^o = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + \text{constant} \qquad \ln\left(\frac{P_2^o}{P_1^o}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{K_{T2}}{K_{T1}}\right) = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln P^o(L) \cong 19\left(1 - \frac{T_b}{T}\right) + 8.5\left(\ln \frac{T_b}{T}\right) \text{ atm} \qquad \ln \frac{P^o(s)}{P^o(L)} \cong -6.8\left(\frac{T_m}{T} - 1\right)$$

$$C_w^{sat}(L) = \frac{1}{\overline{V}_{H2O}\ \gamma_w^{sat}} \text{ M}$$

$$C_w^{sat}(s) = C_w^{sat}(L)\ \frac{P^o(s)}{P^o(L)} \qquad C_w^{1atm}(g) = C_w^{sat}(L)\ \frac{1\text{atm}}{P^o(L)}$$

$$\log C_{w,\,salt}^{sat} = \log C_w^{sat} - K^s\ [salt]_{tot}$$

$$K_H \gg K_H^{sat} = \frac{P^o}{C_w^{sat}} = \frac{P^o(L)}{C_w^{sat}(L)} = \overline{V}_{H2O}\ \gamma_w^{sat}\ P^o(L)$$

$$K_{aw} = K_H' = \frac{C_g}{C_w} = \frac{K_H}{RT} \qquad f_g = \frac{V_g}{V_g + \frac{1}{K_H'}V_w} \qquad \text{where } K_H' = K_{aw} \text{ (unitless)}$$

$$K_H^{salt} = K_H\, 10^{K^s [salt]_{tot}}$$

$$K_{ow} = \frac{C_{octanol}}{C_{water}} = \frac{\gamma_w^{sat}\ \overline{V}_{H2O}}{\gamma_{oct}^{sat}\ \overline{V}_{oct}}$$

$$\log\left\{\frac{K_{aX}}{K_{aH}}\right\} \equiv \sigma \text{ (for BAs)} \qquad \log\left\{\frac{K_X}{K_H}\right\} = \rho\Sigma\sigma \qquad \log\left\{\frac{k_X}{k_H}\right\} = \rho\Sigma\sigma$$

$$\log\left(\frac{k_{Nu}}{k_{H2O}}\right) \equiv n \quad \text{(for } CH_3Br\text{)} \qquad \log\left(\frac{k_{Nu}}{k_{H2O}}\right) = n\,s$$

$$\alpha_{HA} = \frac{[HA]}{[HA] + [A^-]} = \frac{1}{1 + \frac{K_a}{[H^+]}} = \frac{1}{1 + 10^{(pH - pKa)}}$$

$$\ln \gamma_w = -\ln P^o(L) + s\left[V^{2/3}\left(\frac{n_D^{\ 2} - 1}{n_D^{\ 2} + 2}\right)\right] + a\,(\alpha) + b\,(\beta) + v\,\overline{V} + \text{Constant}$$

Information

Molar Volumes:

$$\overline{V}_{H2O} = 0.018\,\text{L mol}^{-1}$$

$$\overline{V}_{octanol} = 0.13\,\text{L mol}^{-1}$$

Table 1: Hammett constants for some common substituents

Substituent	σ_{meta}	σ_{para}	σ^-	σ^+	$\sigma_o^{phenols}$
CH_3	-0.07	-0.17		-0.31	-0.13
Ph (C_6H_5)	0.06	0.01			
Cl	0.37	0.23		0.11	0.68
Br	0.39	0.23	0.26	0.15	0.70
I	0.35	0.18		0.13	0.63
OH	0.10	-0.37		-0.92	
OCH_3	0.12	-0.27	-0.12	-0.78	0.0
NO_2	0.71	0.78	1.25	0.79	1.24
CN	0.56	0.66	0.89	0.66	
CO_2CH_3	0.33	0.45	0.66		
$OCOCH_3$	0.36	0.31			
NH_2	-0.16	-0.66		-1.3	
$N(CH_3)_2$	-0.15	-0.83			

Note: σ^- and σ^+ apply to *para* substituted groups only

Table 2: Reaction and acidity constants for aromatic acids in water at 25°C

Acid	ρ	pK_{aH}
Benzoic acid	1.00	4.19
Phenol	2.25	9.92
Phenoxy acetic acid	0.30	3.17
2-Chlorophenoxy acetic acid	0.30	3.05
Conjugate acid of aniline	2.89	4.63

Table 3: Structural Unit Contributions to Calculate the log K_H'

Bond	Contribution	Bond	Contribution
C-H	+0.12	C_{ar}-H	+0.15
C-F	+0.42	C_{ar}-Cl	+0.02
C-Cl	-0.33	C_{ar}-Br	-0.25
C-Br	-0.82	C_{ar}-O	+0.35
C-I	-1.01	C_{ar}-S	-0.63
C-O	-1.09	C_{ar}-C_{ar}	-0.26
C-S	-1.11	C_{ar}-N_{ar}	-1.63
C-N	-1.30	=C-H	+0.10
C-C	-0.12	=C-Cl	-0.04
C-C=	-0.06	C=C	-0.10
C-C≡	-0.54	≡C-H	0.00
C-C_{ar}	-0.16	S-H	-0.23
O-H	-3.23	N-H	-1.28

Table 4: Swain-Scott nucleophilicities based on reaction with methyl bromide.

Nucleophile	*n*	Nucleophile	*n*
ClO_4^-	< 0	HPO_4^{2-}	3.8
H_2O	0.0	Br^-	3.9
NO_3^-	1.0	OH^-	4.2
F^-	2.0	I^-	5.0
SO_4^{2-}	2.5	CN^-	5.1
CH_3COO^-	2.7	HS^-	5.1
Cl^-	3.0	SO_3^{2-}	5.1
HCO_3^-	3.8	S_4^{2-}	7.1