Data Sheet – BCH341 – Tinoco - BioThermodynamics

Table 1 – Thermodynamic Data for Selected Compounds and Elements at 1 bar and 298K.

Substance	$\Delta_f H^o$ (kJ mol^{-1})	S^o (J K^{-1} mol^{-1})	C_P^o (J K^{-1} mol^{-1})	$\Delta_f G^o$ (kJ mol^{-1})
Ag (*s*)	0	42.55	25.4	0
Ag^+ (*aq*)	105.8	73.45	-	76.8
AgCl (*s*)	-127.0	96.3	-	109.8
$AlCl_3$ (*s*)	-704.2	110.7	91.84	-628.8
Ar (*g*)	0	154.8	20.8	
C (*g*)	716.7	158.2	-	669.2
C (*s, graphite*)	0	5.7	8.52	0
C (*s, diamond*)	1.9	2.4	6.11	2.9
$CaCO_3$ (*s, calcite*)	-1206.9	92.9	-	-1128.8
Cl_2 (*g*)	0	223.2	-	0
Cl- (*aq*)	-167.2	56.5	-	-131.2
CO (*g*)	-110.5	197.8	29.1	-137.0
CO_2 (*g*)	-393.5	213.8	37.1	-394.4
CO_2 (*aq*)	-413.8	117.6	-	-386.0
HCO_3^- (*aq*)				
Fe (*s*)	0	27.28	25.1	0
Fe^{3+} (*aq*)	-48.5	-315.9	-	-10.6
H_2 (*g*)	0	130.8	28.8	0
H_2SO_4 (*g*)	-814.0	156.9	138.9	-690.0
H_2O (*g*)	-241.8	188.7	33.6	-228.7
H_2O (*l*)	-285.8	69.9	75.3	-237.1
H_2O (*s*)	-292.0	20.0	36.0	
H^+ (*aq*)	0	0		0
OH^- (*aq*)	-230.0	-10.8	-	-157.2
H_2O_2 (*aq*)	-191.2	143.9	-	-134.0
Li^+ (*aq*)	-278.5	14.23	-	-293.8
$MgCO_3$ (*s*)	-1095.8	65.7	75.5	-1012.1
MgO (*s*)	-601.8	30.8	37.4	-569.6
N_2 (*g*)	0	191.6	29.1	
N_2H_4 (*l*)	50.6	121.2	139.3	
NH_3 (*g*)	-46.1	192.6	35.7	-16.8
NH_3 (*aq*)	-80.3	111.3	-	-26.5
NO (*g*)	90.4	210.6	29.9	
NO_2 (*g*)	33.9	240.5	37.9	
N_2O_4 (*g*)	9.7	304.3	79.1	
Na+ (aq)	-240.1	59.0	-	-261.9
O_2 (*g*)	0	205.0	29.4	
O (*g*)	249.17	161.1	21.9	
S(*s, rhombic*)	0	31.80	22.6	
SO_2 (*g*)	-296.8	248.2	39.9	-300.1
SO_3 (*g*)	-395.7	256.8	50.7	-370.4
Xe (*g*)	0	169.6	20.8	0
n-Butane	-125.6	310.2	-	-16.3
Ethylene (C_2H_4) (*g*)	52.5	219.3	43.6	68.5
Ethane (C_2H_6) (*g*)	-84.0	229.7	52.7	-32.1
L-Glycine (*s*)	-528.5	103.5	99.2	-373.4
Glucose ($C_6H_{12}O_6$)	-1274.4	212.1	-	-917.4
n-Hexane	-167.1	388.9	-	0.17
Isobutane	-134.2	294.8	-	-20.3
Methane	-74.9	186.3	-	-50.7
Sucrose (($C_{12}H_{22}O_{11}$)	-2222.1	360.2	-	-119.3

Useful Equations & Mathematical Relations:

$F_{sp} = -F_{ex} = -k(x-x_o)$ $\quad w = \int F_{ex}(x)\ dx = \int -k(x-x_o)\,dx$

$$w = \int F_{ex}(x)\ dx = \int mg\,dx \approx mg\int dx = mgh$$

$PV = nRT$ $\quad$ Pressure=F/A = gm/A

$P_i = \chi_i P_T$ $\quad dq = Cdt$

$\chi_i = \frac{n_i}{\sum_i n_i}$ $\quad \left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$

$w = -nRT\ ln\left({}^{V_2}/_{V_1}\right)$ $\quad \Delta U = q + w$

$dU = \partial q + \partial w$ $\quad H \equiv U + PV$

$C_V = \left(\frac{\partial U}{\partial T}\right)_V$ $\quad C_P = \left(\frac{\partial H}{\partial T}\right)_P$

$dH = C_P dT$ $\quad \Delta H = nC_P\Delta T$

$C_V = {}^3/_2\,R$ $\quad C_P - C_V = R$

$P_1V_1 = P_2V_2$ $\quad w = nC_V\Delta T$

$\Delta_r H^o(T') = \Delta_r H^o(T) + \Delta_r C_P^o(T'-T)$

$\Delta_r H^o = \sum \nu \Delta_f H^o$ (products) - $\sum \nu \Delta_f H^o$ (reactants)

$\Delta_r C_P^o = \sum \nu C_p^o$ (products) - $\sum \nu C_p^o$ (reactants)

$\Delta_r S^o = \sum \nu S_m^o$ (products) - $\sum \nu S_m^o$ (reactants)

$\Delta_r G^o = \sum \nu G_m^o$ (products) - $\sum \nu G_m^o$ (reactants)

$S = k_B ln W$ $\quad \Delta S = nR\ ln\left(\frac{V_2}{V_1}\right)$

$\Delta S = \frac{q_{rev}}{T}$ $\quad dS = \frac{dq_{rev}}{T}$

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \geq 0$ $\quad \Delta S_{mix} = -nR(\chi_A ln\ \chi_A + \chi_B ln\ \chi_B)$

$\Delta_{fus}S = \frac{\Delta_{fus}H}{T_{fus}}$ $\quad \Delta_{vap}S = \frac{\Delta_{vap}H}{T_{b.p.}}$

$\Delta S = nC_P\ ln\left({}^{T_2}/_{T_1}\right)$ $\quad G \equiv U + PV - TS = H - TS$

$\Delta G = \Delta H - T\Delta S$ $\quad dU = TdS - PdV$

$dG = VdP - SdT$ $\quad \Delta G = nRT\ ln\left({}^{P_2}/_{P_1}\right)$

$ln\left({}^{P_2}/_{P_1}\right) = -\frac{\Delta H_{vap}}{R}\left({}^1/_{T_2} - {}^1/_{T_1}\right)$ $\quad G_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{i\neq i}}$

$G_i = \mu_i$

Work=force x distance $\quad$ P=ρgh

ρ=m/V $\quad$ F=ma

$E_K = 1/2mv^2$ $\quad w = -P_{ex}\Delta V$

q = heat = CΔT $\quad \Delta H = \Delta U + \Delta(PV)$

ΔU = w + q $\quad$ dU = dq + dw = TdS – PdV

$dS \geq q/T$ (most general statement of the 2nd law)

$\Delta G = nG_m(2) - nG_m(1)$ $\Delta G_{mix} = nRT(\chi_A \ln \chi_A + \chi_B \ln \chi_B)$

$\chi_j = n_j/n$ $P_j = \chi_j P$

$M = \rho RT/P$ $P_B = \chi_B K_B$

$\Delta_r G = \Delta_r G^\theta + RT \ln Q$ $\Delta_r G^\theta = -RT \ln K$

$\Delta_r G^o = \Delta_r H^o - T\Delta_r S^o$ $\Delta G^o = -RT\ lnK_P$

$\Delta_r G^\theta = \sum \nu G_m{}^o$ (products) - $\sum \nu G_m{}^o$ (reactants)

$\Delta G = \Delta G^o + RT\ lnQ$ $ln\left({}^{K_2}/_{K_1}\right) = -\frac{\Delta_r H^o}{R}\left({}^{1}/_{T_2} - {}^{1}/_{T_1}\right)$

$\left[\frac{\partial ln(K)}{\partial(1/T)}\right]_P = -\frac{\Delta_r H^o}{R}$ $\mu_A = \mu_A^o + RTlna_A$

$pH = pK_A + log\frac{c_s}{c_A}$ $\log \gamma_i = -0.509 Z_i^2 \sqrt{I}$

$I = \frac{1}{2}\sum_i c_i Z_i^2$ $\frac{N_i}{N} = \frac{g_i e^{-E_i/k_B T}}{Q}$

$Q = \sum_i g_i e^{-E_i/k_B T} = partion\ function$ $S = k \ln W$

$\langle h^2 \rangle = Nl^2$ $\langle R^2 \rangle = \frac{Nl^2}{6}$ (open-ended random coil)

$\langle R^2 \rangle = \frac{Nl^2}{12}$ (circular random coil) $\frac{\nu}{[A]} = k(N - \nu)$

$\frac{f}{1-f} = K[A]$ $\frac{d \log[\frac{f}{1-f}]}{d \log[A]} = N$

$F = C - P + 2$ $\lim_{\chi_A \to 1}\left(\frac{P_{vap}}{P^o_{vap}}\right) = \chi_A$

$\mu = \mu^o + RT \ln P_{vap}$ $\mu = \mu^o + RT \ln\left(\frac{P_{vap}}{P^o}\right)$

$\mu_A = \mu_A^o + RT \ln \chi_A$ $\Pi = \frac{RT}{V} n_B = cRT = \frac{w}{M} RT$

$T_f^o - T_f = K_f m$ $T_b - T_b^o = K_b m$

$\mu_A = \mu_A^o + RT \ln a_{xA}$ $a_{xA} = \gamma_A \chi_A$

Conversion Factors:

1 N = 1 kg m s^{-2} 1 Pa = 1 kg m^{-1} s^{-2} = N / m^2

1 J = N m =1 kg m^2 s^{-2} 1 bar ≈ 1 atm

1 atm = 760 torr 1 atm = 760 mm Hg

T(K)=T(°C)+273.15 R = 0.08206 atm(L)/mol(K) = 8.3145 J mol^{-1} K^{-1}

k_B=1.38x10^{-23} J/K 1 L atm = 101.34 J

1L = 1x10^{-3} m^3 N_A = 6.02214x10^{23}

1 bar = 1x10^5 Pa 1 cal = 4.184 J

F = 96485 C/mol c = 2.998x10^8 m/s

RT/F = 25.693 mV 1 eV = 8065.5 cm^{-1}

e = 2.71828 π = 3.14159

e = 1.6x10^{-19} C h = 6.626x10^{-34} J s

ε_o = 8.854x10^{-12} C^2/J m A = 0.509 (water, Debye-Huckel constant)

$g = 9.8\ m/s^2$

Mathematical Relationships:

$\ln x = \ln 10 * \log x \approx 2.3 \log x$

$\ln x + \ln y = \ln xy$ $\quad\quad$ $\ln x - \ln y = \ln(x/y)$

$d \ln x / dx = 1/x$ $\quad\quad$ $d(f+g) = df + dg$

$d(fg) = f dg + g df$ $\quad\quad$ $d(f/g) = 1/g\ df = f/g^2\ dg$

$\int x^n\ dx = (x^{n+1}) / (n+1) + \text{constant}$ $\quad\quad$ $\int 1/x = \ln x + \text{constant}$

$\ln N! = N \ln N - N$

Compound	Ionizing species*	pK^t	$\Delta_r H°$(kJ mol^{-1})
Acetic acid	$HOAc \rightarrow H^+ + OAc$	4.76	−0.08
Adenosine	$AH^+ \rightarrow A = H^+$	3.5	13.0
5'-Adenylic acid	$pAH^+ \rightarrow pA = H^+$	3.7	17.6
(adenosine 5'-phosphate)	$pA \rightarrow pA^- + H^+$	6.4	−7.5
	$pA^- \rightarrow pA^{2-} + H^+$	13.1	45.6
Adenosine triphosphate (ATP)	$pppAH^+ \rightarrow pppA + H^+$	4.0	15.5
	$pppA \rightarrow pppA^- + H^+$	7.0	−5.0
Alanine	$^+H_3NRCOOH \rightarrow {}^+H_3NRCOO + H^+$	2.34	2.9
	$^+H_3NRCOO^- \rightarrow {}^+H_2NRCOO + H^+$	9.87	45.2
Ammonia	$NH_4^+ \rightarrow NH_3 + H^+$	9.24	52.2
Aspartic acid	$^+H_3NRCOOH \rightarrow {}^+H_3NRHCOO + H^+$	2.05	7.5
	$^+H_3NRHCOO^- \rightarrow {}^+H_3NR^-COO^- + H^+$	3.87	4.2
	$^+H_3NR^-COO^- \rightarrow {}^+H_2NR^-COO^- + H^+$	10.0	38.5
Carbonic acid	$H_2CO_3 \rightarrow HCO_3^- + H^+$	6.36	7.66
	$HCO_3 \rightarrow CO_3^{2-} + H^+$	10.24	14.85
Fumaric acid	$R(COOH)_2 \rightarrow {}^-OOCRCOOH + H^+$	3.10	0.4
	$^-OOCROOH \rightarrow {}^-OOCRCOO^- + H^+$	4.6	−2.9
Glycine	$^+H_3NRCOOH \rightarrow {}^+H_3NRCOO^- + H^+$	2.35	3.92
	$^+H_3NRCOO^- \rightarrow {}^+H_2NRCOO^- + H^+$	9.78	44.2
Histidine	$^+H_3NRH^+COOH \rightarrow {}^+H_3NRH^+COO^- + H^+$	1.80	—
	$^+H_3NRH^+COO^- \rightarrow {}^+H_3NRCOO^- + H^+$	6.04	29.9
	$^+H_3NRCOO^- \rightarrow {}^+H_2NRCOO^- + H^+$	9.33	46.6
Hydrocyanic acid	$HCN \rightarrow CN^- + H^+$	9.21	43.5
Lysine	$^+H_3NRH^+COOH \rightarrow {}^+H_3NRH^+COO^- + H^+$	2.16	1.26
	$^+H_3NRH^+COO^- \rightarrow {}^+H_3NRCOO^- + H^+$	9.06	53.6
	$^+H_3NRCOO^- \rightarrow {}^+H_2NRCOO^- + H^+$	10.53	48.5
Phenol	$ROH \rightarrow RO^- + H^+$	9.98	23.6
Phosphoric acid	$H_3PO_4 \rightarrow H_2PO_4^- + H^+$	2.16	−7.95
	$H_2PO_4^- \rightarrow HPO_4^{2-} + H^+$	7.21	4.15
	$HPO_4^{2-} \rightarrow PO_4^{3-} + H^+$	12.32	14.7
Pyruvic acid	$RCOOH \rightarrow RCOO^- + H^+$	2.49	12.1
Tyrosine	$^+H_3NRHCOOH \rightarrow {}^+H_3NRHCOO^- + H^+$	2.20	—
	$^+H_3NRHCOO^- \rightarrow {}^+H_3NR^-COO^- + H^+$	9.11	—
	$^+H_3NR^-COO^- \rightarrow H_2NR^-COO^- + H^+$	10.1	25.1
Water	$H_2O \rightarrow OH^- + H^+$	14.00	55.82

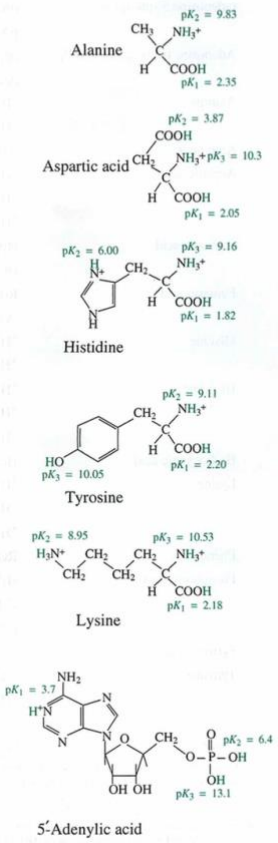

FIGURE 4.11 The p*K* values from table 4.2 of several amino acids and of a nucleotide; $pK = -\log K$.

TABLE 4.4 Thermodynamic parameters* for calculating double-strand stability in DNA (pH 7, 1 M Nacl)

	$\Delta_r G°$ (kJ mol^{-1}) at 37°C	$\Delta_r H°$(kJ mol^{-1})	$\Delta_r S°$(JK^{-1} mol^{-1})
5′-AA-3′ / 3′-TT-5′	−4.2	−33.1	−93.0
5′-AT-3′ / 3′-TA-5′	−3.7	−30.2	−85.4
5′-TA-3′ / 3′-AT-5′	−2.4	−30.2	−89.2
5′-AC-3′ / 3′-TG-5′	−6.0	−35.2	−93.8
5′-CA-3′ / 3′-GT-5′	−6.0	−35.6	−95.0
5′-AG-3′ / 3′-TC-5′	−5.4	−32.7	−87.9
5′-GA-3′ / 3′-CT-5′	−5.4	−34.3	−93.0
5′-GG-3′ / 3′-CC-5′	−9.1	−44.4	−113.9
5′-CG-3′ / 3′-GC-5′	−9.3	−41.0	−102.2
5′-CC-3′ / 3′-GG-5′	−7.7	−33.5	−83.3

The initial interaction of two strands contributes a loss of entropy and an unfavorable free energy that must be included in calculations:
$\Delta_r G°$(initiation) = +8.1 kJ mol^{-1}, $\Delta_r S°$(initiation) = −23.4 J K^{-1} mol^{-1}, $\Delta_r H°$(initiation) = +0.8 kJ mol^{-1}.
*Based on data from H. T. Allawai and J. SantaLucia Jr., "Thermodynamics and NMR of Internal G-T Mismatches in DNA", *Biochemistry* 36, 10581–10594. Copyright © 1997 American Chemical Society.

TABLE 6.1 Henry's Law coefficients $k_B = p_{v,B}/x_B$, in bar, for aqueous solutions

Gas	0°C	25°C	37°C
He	131×10^3	139×10^3	138×10^3
N_2	50×10^3	84×10^3	98×10^3
CO	35×10^3	57×10^3	67×10^3
O_2	26×10^3	42×10^3	50×10^3
CH_4	23×10^3	38×10^3	46×10^3
Ar	24×10^3	38×10^3	45×10^3
CO_2	0.71×10^3	1.59×10^3	2.13×10^3
C_2H_2	0.71×10^3	1.32×10^3	1.69×10^3

Source: Based on data from Harvey, A. H., "Semiempirical correlation for Henry's constants over large temperature ranges," *AIChE Journal*, 42, pp. 1491–1494. DOI: 10.1002/aic.690420531. Copyright (c) 1966 John Wiley and Sons, Inc.

TABLE 6.4 Thermodynamic data for the transfer of hydrocarbons to water at 25°C

Hydrocarbon	$\Delta\mu^\circ$ (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
C_2H_6	16.3	−10.5	−88
C_3H_8	20.5	−7.1	−92
C_4H_{10}	24.7	−3.3	−96
C_5H_{12}	28.6	−2.0	−103
C_6H_{14}	32.6	0	−109
C_6H_6	19.3	+2.1	−58
$C_6H_5CH_3$	22.8	+1.7	−71
$C_6H_5C_2H_5$	26.2	+2.0	−81
$C_6H_5C_3H_7$	28.8	+2.3	−89

Source: Based on data from C. Tanford, *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, 2nd Edition. Copyright (c) 1980 John Wiley and Sons, Inc.

Reaction	$\Delta_r G^{\circ\prime}$ (kJ mol^{-1})
D-Glucose + ATP → D-glucose-6-phosphate + ADP	−16.7
D-Glucose-6-phosphate → D-fructose-6-phosphate	+1.7
D-Fructose-6-phosphate + ATP → D-fructose-1,6-bisphosphate + ADP	−14.2
Fructose-1,6-bisphosphate → dihydroxyacetone phosphate + glyceraldehyde-3-phosphate	+23.8
Dihydroxyacetone phosphate → glyceraldehyde-3-phosphate	+7.5
Glyceraldehyde-3-phosphate + phosphate +NAD^+ → 1,3-bisphosphoglycerate NADH + H^+	+6.3
1,3-Bisphosphoglycerate + ADP → 3-phosphoglycerate + ATP	−18.8
3-Phosphoglycerate → 2-phosphoglycerate	+4.6
2-Phosphoglycerate → phosphoenolypyruvate + H_2O	+1.7
2-Phosphoenolpyruvate + ADP → pyruvate + ATP	−31.4
Pyruvate + NADH + H^+ → lactate + NAD^+	−25.1
Pyruvate → acetaldehyde + CO_2	−19.8
Acetaldehyde + NADH + H^+ → ethanol + NAD^+	−23.7

Pure Solids and liquids

Standard state is the pure substance at 1 bar. The activity is equal to 1 for a pure solid or liquid at 1 bar, and it changes only slightly with pressure:

$$a_A = 1 \tag{4.25}$$

Solvent of a solution

Standard state is the pure solvent at 1 bar. The activity is

$$a_A = \gamma_A x_A . \tag{4.31}$$

Solutes in a Solution

Standard state of a solute is a hypothetical one where the concentration of the solute is equal to 1 molar (M) or 1 molal (m), but the properties are those extrapolated from very dilute solutions:

$$a_B = \gamma_B c_B \quad (\gamma_B \rightarrow 1 \quad \text{as} \quad c_B \rightarrow 0) \tag{4.35}$$

$$a_B = \gamma_B m_B \quad (\gamma_B \rightarrow 1 \quad \text{as} \quad m_B \rightarrow 0) \tag{4.41}$$

Ions

The Debye–Hückel Limiting Law for the activity coefficient of an ion in water at 25 °C:

$$\log \gamma_{ion} = -0.509\ Z_i^2 I^{1/2} \tag{4.47}$$

Z_i = charge on ion ($\pm 1, \pm 2, \pm 3$, etc.)

$$I = \text{ionic strength} = \frac{1}{2}\sum_i c_i Z_i^2 \tag{4.43}$$

Biochemical Standard State

At pH 7, $a_{H^+} = 1$; the activity of each of the other species is set equal to the *total concentration* of all species of that molecule at pH 7.0:

$$a_A = \sum_{\text{species } i} c_{i,A} \quad (\text{at pH } 7.0) \tag{4.42}$$

ΔG and the Equilibrium Constant for a Chemical Reaction

$$aA + bB \rightarrow cC + dD$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q \tag{4.20}$$

$\Delta_r G$= Gibbs free-energy change for the reaction at T and concentrations specified in Q.
$\Delta_r G^\circ$= standard Gibbs free-energy change for the reaction at T with all reactants and products at their standard states.

Q	=	$\dfrac{(a_C)^c (a_D)^d}{(a_B^{eq})^b (a_A^{eq})^a}$	(4.14)
a_A, a_B, a_C, a_D	=	activities of reactants and products at the concentrations specified	

$\Delta_r G^\circ$	=	$-RT \ln K$	
K	=	equilibrium constant	
	=	$\dfrac{(a_C^{eq})^c (a_D^{eq})^d}{(a_B^{eq})^b (a_A^{eq})^a}$	(4.22)
a_A^{eq}, etc.	=	activities of reactants and products at equilibrium	

$2.3026RT$ = 5708 J mol^{-1} at 298 K ($K = e^{-\Delta_r G^\circ/RT} = 10^{-\Delta_r G^\circ/2.303RT}$)