THERMODYNAMIC QUANTITIES FOR THE IONIZATION REACTIONS OF BUFFERS IN WATER

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This table contains selected values for the pK, standard molar enthalpy of reaction $\Delta_r H^\circ$, and standard molar heat-capacity change $\Delta_r C_p^\circ$ for the ionization reactions of 64 buffers many of which are relevant to biochemistry and to biology.[1] The values pertain to the temperature T = 298.15 K and the pressure p = 0.1 MPa. The standard state is the hypothetical ideal solution of unit molality. These data permit one to calculate values of the pK and of $\Delta_r H^\circ$ at temperatures in the vicinity $\{T \approx (274\ \text{K to}\ 350\ \text{K})\}$ of the reference temperature θ = 298.15 K by using the following equations[2]

$$\Delta_r G^\circ_T = -RT\ln K_T = \ln(10)\cdot RT\cdot \mathrm{p}K_T\ , \qquad (1)$$

$$R\ln K_T = -(\Delta_r G^\circ_\theta/\theta) + \Delta_r H^\circ_\theta\{(1/\theta) - (1/T)\} + \Delta_r C^\circ_{p\theta}\{(\theta/T) - 1 + \ln(T/\theta)\}, \qquad (2)$$

$$\Delta_r H^\circ_T = \Delta_r H^\circ_\theta + \Delta_r C^\circ_{p\theta}(T-\theta). \qquad (3)$$

Here, $\Delta_r G^\circ$ is the standard molar Gibbs energy change and K is the equilibrium constant for a reaction; R is the gas constant (8.314 472 J K^{-1} mol^{-1}). The subscripts T and θ denote the temperature to which a quantity pertains, the subscript p denotes constant pressure, and the subscript r denotes that the quantity refers to a reaction. Combination of equations (1) and (2) yields the following equation that gives pK as a function of temperature:

$$\mathrm{p}K_T = -\{R\cdot\ln(10)\}^{-1}[-\{\ln(10)\cdot RT\cdot \mathrm{p}K_\theta/\theta\} + \Delta_r H^\circ_\theta\{(1/\theta) - (1/T)\} + \Delta_r C^\circ_{p\theta}\{(\theta/T) - 1 + \ln(T/\theta)\}]. \qquad (4)$$

The above equations neglect higher order terms that involve temperature derivatives of $\Delta_r C^\circ_p$. Also, it is important to recognize that the values of pK and $\Delta_r H^\circ$ effectively pertain to ionic strength I = 0. However, the values of pK and $\Delta_r H^\circ$ are almost always dependent on the ionic strength and the actual composition of the solution. These issues are discussed in Reference 1 which also gives an approximate method for making appropriate corrections.

References

1. Goldberg, R. N., Kishore, N., and Lennen, R. M., "Thermodynamic Quantities for the Ionization Reactions of Buffers," *J. Phys. Chem. Ref. Data*, in press.
2. Clarke, E. C. W., and Glew, D. N., *Trans. Faraday Soc.*, 62, 539-547, 1966.

Selected Values of Thermodynamic Quantities for the Ionization Reactions of Buffers in Water at T = 298.15 K and p = 0.1 MPa

			$\Delta_r H^\circ$	$\Delta_r C_p^\circ$
Buffer	**Reaction**	**pK**	**kJ mol^{-1}**	**J K^{-1} mol^{-1}**
ACES	$HL^\pm = H^+ + L^-$, ($HL = C_4H_{10}N_2O_4S$)	6.847	30.43	−49
Acetate	$HL = H^+ + L^-$, ($HL = C_2H_4O_2$)	4.756	−0.41	−142
ADA	$H_3L^+ = H^+ + H_2L^\pm$, ($H_2L = C_6H_{10}N_2O_5$)	1.59		
	$H_2L^\pm = H^+ + HL^-$	2.48	16.7	
	$HL^- = H^+ + L^{2-}$	6.844	12.23	−144
2-Amino-2-methyl-1,3-propanediol	$HL^+ = H^+ + L$, ($L = C_4H_{11}NO_2$)	8.801	49.85	−44
2-Amino-2-methyl-1-propanol	$HL^+ = H^+ + L$, ($L = C_4H_{11}NO$)	9.694	54.05	≈−21
3-Amino-1-propanesulfonic acid	$HL = H^+ + L^-$, ($HL = C_3H_9NO_3S$)	10.2		
Ammonia	$NH_4^+ = H^+ + NH_3$	9.245	51.95	8
AMPSO	$HL^\pm = H^+ + L^-$, ($HL = C_7H_{17}NO_5S$)	9.138	43.19	−61
Arsenate	$H_3AsO_4 = H^+ + H_2AsO_4^-$	2.31	−7.8	
	$H_2AsO_4^- = H^+ + HAsO_4^{2-}$	7.05	1.7	
	$HAsO_4^{2-} = H^+ + AsO_4^{3-}$	11.9	15.9	
Barbital	$H_2L = H^+ + HL^-$, ($H_2L = C_8H_{12}N_2O_3$)	7.980	24.27	−135
	$HL^- = H^+ + L^{2-}$	12.8		
BES	$HL^\pm = H^+ + L^-$, ($HL = C_6H_{15}NO_5S$)	7.187	24.25	−2
Bicine	$H_2L^+ = H^+ + HL^\pm$, ($HL = C_6H_{13}NO_4$)	2.0		
	$HL^\pm = H^+ + L^-$	8.334	26.34	0
Bis-tris	$H_3L^+ = H^+ + H_2L^\pm$, ($H_2L = C_8H_{19}NO_5$)	6.484	28.4	27
Bis-tris propane	$H_2L^{2+} = H^+ + HL^+$, ($L = C_{11}H_{26}N_2O_6$)	6.65		
	$HL^+ = H^+ + L$	9.10		
Borate	$H_3BO_3 = H^+ + H_2BO_3^-$	9.237	13.8	≈−240
Cacodylate	$H_2L^+ = H^+ + HL$, ($HL = C_2H_6AsO_2$)	1.78	−3.5	
	$HL = H^+ + L^-$	6.28	−3.0	−86
CAPS	$HL^\pm = H^+ + L^-$, ($HL = C_9H_{19}NO_3S$)	10.499	48.1	57
CAPSO	$HL^\pm = H^+ + L^-$, ($HL = C_9H_{19}NO_4S$)	9.825	46.67	21
Carbonate	$H_2CO_3 = H^+ + HCO_3^-$	6.351	9.15	−371
	$HCO_3^- = H^+ + CO_3^{2-}$	10.329	14.70	−249
CHES	$HL^\pm = H^+ + L^-$, ($HL = C_8H_{17}NO_3S$)	9.394	39.55	9

Buffer	Reaction	pK	$\Delta_r H^\circ$ kJ mol^{-1}	$\Delta_r C_p^\circ$ J K^{-1} mol^{-1}
Citrate	$H_3L = H^+ + H_2L^-$, ($H_3L = C_6H_8O_7$)	3.128	4.07	−131
	$H_2L^- = H^+ + HL^{2-}$	4.761	2.23	−178
	$HL^{2-} = H^+ + L^{3-}$	6.396	−3.38	−254
L-Cysteine	$H_3L^+ = H^+ + H_2L$, ($H_2L = C_3H_7NO_2S$)	1.71	≈−0.6	
	$H_2L = H^+ + HL^-$	8.36	36.1	≈−66
	$HL^- = H^+ + L^{2-}$	10.75	34.1	≈−204
Diethanolamine	$HL^+ = H^+ + L$, ($L = C_4H_{11}NO_2$)	8.883	42.08	36
Diglycolate	$H_2L = H^+ + HL^-$, ($H_2L = C_4H_6O_5$)	3.05	−0.1	≈−142
	$HL^- = H^+ + L^{2-}$	4.37	−7.2	≈−138
3,3-Dimethylglutarate	$H_2L = H^+ + HL^-$, ($H_2L = C_7H_{12}O_4$)	3.70		
	$HL^- = H^+ + L^{2-}$	6.34		
DIPSO	$HL^\pm = H^+ + L^-$, ($HL = C_7H_{17}NO_6S$)	7.576	30.18	42
Ethanolamine	$HL^+ = H^+ + L$, ($L = C_2H_7NO$)	9.498	50.52	26
N-Ethylmorpholine	$HL^+ = H^+ + L$, ($L = C_6H_{13}NO$)	7.77	27.4	
Glycerol 2-phosphate	$H_2L = H^+ + HL^-$, ($H_2L = C_3H_9NO_6P$)	1.329	−12.2	−330
	$HL^- = H^+ + L^{2-}$	6.650	−1.85	−212
Glycine	$H_2L^+ = H^+ + HL^\pm$, ($HL = C_2H_5NO_2$)	2.351	4.00	−139
	$HL^\pm = H^+ + L^-$	9.780	44.2	−57
Glycine amide	$HL^+ = H^+ + L$, ($L = C_2H_6N_2O$)	8.04	42.9	
Glycylglycine	$H_2L^+ = H^+ + HL^\pm$, ($HL = C_4H_8N_2O_3$)	3.140	0.11	−128
	$HL^\pm = H^+ + L^-$	8.265	43.4	−16
Glycylglycylglycine	$H_2L^+ = H^+ + HL^\pm$, ($HL = C_6H_{11}N_3O_4$)	3.224	0.84	
	$HL^\pm = H^+ + L^-$	8.090	41.7	
HEPES	$H_2L^+ = H^+ + HL^\pm$, ($HL = C_8H_{18}N_2O_4S$)	≈3.0		
	$HL^\pm = H^+ + L^-$	7.564	20.4	47
HEPPS	$HL^\pm = H^+ + L^-$, ($HL = C_6H_{20}N_2O_4S$)	7.957	21.3	48
HEPPSO	$HL^\pm = H^+ + L^-$, ($HL = C_9H_{20}N_2O_5S$)	8.042	23.70	47
L-Histidine	$H_3L^{2+} = H^+ + H_2L^+$, ($HL = C_6H_9N_3O_2$)	1.5_4	3.6	
	$H_2L^+ = H^+ + HL$	6.07	29.5	176
	$HL = H^+ + L^-$	9.34	43.8	−233
Hydrazine	$H_2L^{2+} = H^+ + HL^+$, ($L = H_4N_2$)	−0.99	38.1	
	$HL^+ = H^+ + L$	8.02	41.7	
Imidazole	$HL^+ = H^+ + L$, ($L = C_3H_4N_2$)	6.993	36.64	−9
Maleate	$H_2L = H^+ + HL^-$, ($H_2L = C_4H_4O_4$)	1.92	1.1	≈−21
	$HL^- = H^+ + L^{2-}$	6.27	−3.6	≈−31
2-Mercaptoethanol	$HL = H^+ + L^-$, ($HL = C_2H_6OS$)	9.7_5	26.2	
MES	$HL^\pm = H^+ + L^-$, ($HL = C_6H_{13}NO_4S$)	6.270	14.8	5
Methylamine	$HL^+ = H^+ + L$, ($L = CH_5N$)	10.645	55.34	33
2-Methylimidazole	$HL^+ = H^+ + L$, ($L = C_4H_6N_2$)	8.0_1	36.8	
MOPS	$HL^\pm = H^+ + L^-$, ($HL = C_7H_{15}NO_4S$)	7.184	21.1	25
MOPSO	$H_2L^+ = H^+ + HL^\pm$, ($HL = C_7H_{15}NO_5S$)	0.060		
	$HL^\pm = H^+ + L^-$	6.90	25.0	≈38
Oxalate	$H_2L = H^+ + HL^-$, ($H_2L = C_2H_2O_4$)	1.27	−3.9	≈−231
	$HL^- = H^+ + L^{2-}$	4.266	7.00	−231
Phosphate	$H_3PO_4 = H^+ + H_2PO_4^-$	2.148	−8.0	−141
	$H_2PO_4^- = H^+ + HPO_4^{2-}$	7.198	3.6	−230
	$HPO_4^{2-} = H^+ + PO_4^{3-}$	12.35	16.0	−242
Phthalate	$H_2L = H^+ + HL^-$, ($H_2L = C_8H_6O_4$)	2.950	−2.70	−91
	$HL^- = H^+ + L^{2-}$	5.408	−2.17	−295
Piperazine	$H_2L^{2+} = H^+ + HL^+$, ($L = C_4H_{10}N_2$)	5.333	31.11	86
	$HL^+ = H^+ + L$	9.731	42.89	75
PIPES	$HL^\pm = H^+ + L^-$, ($HL = C_8H_{18}N_2O_6S_2$)	7.141	11.2	22
POPSO	$HL^\pm = H^+ + L^-$, ($HL = C_{10}H_{22}N_2O_8S_2$)	≈8.0		
Pyrophosphate	$H_4P_2O_7 = H^+ + H_3P_2O_7^-$	0.83	−9.2	≈−90
	$H_3P_2O_7^- = H^+ + H_2P_2O_7^{2-}$	2.26	−5.0	≈−130
	$H_2P_2O_7^{2-} = H^+ + HP_2O_7^{3-}$	6.72	0.5	−136
	$HP_2O_7^{3-} = H^+ + P_2O_7^{4-}$	9.46	1.4	−141
Succinate	$H_2L = H^+ + HL^-$, ($H_2L = C_4H_6O_4$)	4.207	3.0	−121
	$HL^- = H^+ + L^{2-}$	5.636	−0.5	−217
Sulfate	$HSO_4^- = H^+ + SO_4^{2-}$	1.987	−22.4	−258

Buffer	Reaction	p*K*	$\Delta_r H^\circ$ kJ mol^{-1}	$\Delta_r C_p^\circ$ J K^{-1} mol^{-1}
Sulfite	$H_2SO_3 = H^+ + HSO_3^-$	1.857	−17.80	−272
	$HSO_3^- = H^+ + SO_3^{2-}$	7.172	−3.65	−262
TAPS	$HL^\pm = H^+ + L^-$, (HL = $C_7H_{17}NO_6S$)	8.44	40.4	15
TAPSO	$HL^\pm = H^+ + L^-$, (HL = $C_7H_{17}NO_7S$)	7.635	39.09	−16
L(+)-Tartaric acid	$H_2L = H^+ + HL^-$, (H_2L = $C_4H_6O_6$)	3.036	3.19	−147
	$HL^- = H^+ + L^{2-}$	4.366	0.93	−218
TES	$HL^\pm = H^+ + L^-$, (HL = $C_6H_{15}NO_6S$)	7.550	32.13	0
Tricine	$H_2L^+ = H^+ + HL^\pm$, (HL = $C_6H_{13}NO_5$)	2.023	5.85	−196
	$HL^\pm = H^+ + L^-$	8.135	31.37	−53
Triethanolamine	$HL^+ = H^+ + L$, (L = $C_6H_{15}NO_3$)	7.762	33.6	50
Triethylamine	$HL^+ = H^+ + L$, (L = $C_6H_{15}N$)	10.72	43.13	151
Tris	$HL^+ = H^+ + L$, (L = $C_4H_{11}NO_3$)	8.072	47.45	−59