# THERMODYNAMIC QUANTITIES FOR THE IONIZATION REACTIONS OF BUFFERS IN WATER

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This table contains selected values for the p$K$, standard molar enthalpy of reaction $\Delta_r H°$, and standard molar heat-capacity change $\Delta_r C_p°$ 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 p$K$ and of $\Delta_r H°$ at temperatures in the vicinity {$T \approx$ (274 K to 350 K)} of the reference temperature $\theta$ = 298.15 K by using the following equations[2]

$$\Delta_r G_T° = -RT \ln K_T = \ln(10) \cdot RT \cdot \mathrm{p}K_T, \quad (1)$$

$$R \ln K_T = -(\Delta_r G_\theta° / \theta) + \Delta_r H_\theta° \{(1/\theta) - (1/T)\} + \Delta_r C°_{p\theta} \{(\theta/T) - 1 + \ln(T/\theta)\}, \quad (2)$$

$$\Delta_r H_T° = \Delta_r H°_\theta + \Delta_r C°_{p\theta} (T - \theta). \quad (3)$$

Here, $\Delta_r G°$ 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 $\theta$ 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 p$K$ as a function of temperature:

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

The above equations neglect higher order terms that involve temperature derivatives of $\Delta_r C_p°$. Also, it is important to recognize that the values of p$K$ and $\Delta_r H°$ effectively pertain to ionic strength $I$ = 0. However, the values of p$K$ and $\Delta_r H°$ 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*, 31, 231, 2002.
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**

| Buffer | Reaction | p$K$ | $\Delta_r H°$ kJ mol$^{-1}$ | $\Delta_r C_p°$ J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|
| 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 | p*K* | $\Delta_r H^\circ$ kJ mol⁻¹ | $\Delta_r C_p^\circ$ J mol⁻¹ K⁻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$K$ | $\Delta_r H°$ kJ mol⁻¹ | $\Delta_r C_p°$ J mol⁻¹ K⁻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 |