

# 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  $\Delta_r C_{p,\theta}^\circ$  for the ionization reactions of 64 buffers many of which are relevant to biochemistry and to biology.<sup>1</sup> 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  $\theta = 298.15$  K by using the following equations<sup>2</sup>

$$\Delta_r G_T^\circ = -RT \ln K_T = \ln(10) \cdot RT \cdot pK_T, \quad (1)$$

$$R \ln K_T = -(\Delta_r G_\theta^\circ / \theta) + \Delta_r H_\theta^\circ \left\{ (1/\theta) - (1/T) \right\} + \Delta_r C_{p,\theta}^\circ \left\{ (\theta/T) - 1 + \ln(T/\theta) \right\}, \quad (2)$$

$$\Delta_r H_T^\circ = \Delta_r H_\theta^\circ + \Delta_r C_{p,\theta}^\circ (T - \theta). \quad (3)$$

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<sup>-1</sup> mol<sup>-1</sup>). The subscripts  $T$  and  $\theta$  denote the temperature to which a quantity pertains, the subscript  $p$  denotes constant pres-

sure, 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:

$$pK_T = -\{R \ln(10)\}^{-1} \left[ -\{\ln(10) \cdot RT \cdot pK_\theta / \theta\} + \Delta_r H_\theta^\circ \left\{ (1/\theta) - (1/T) \right\} + \Delta_r C_{p,\theta}^\circ \left\{ (\theta/T) - 1 + \ln(T/\theta) \right\} \right]. \quad (4)$$

The above equations neglect higher order terms that involve temperature derivatives of  $\Delta_r C_{p,\theta}^\circ$ . 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

Buffer	Reaction	$pK$	$\Delta_r H^\circ$	$\Delta_r C_{p,\theta}^\circ$
			kJ mol <sup>-1</sup>	J K <sup>-1</sup> mol <sup>-1</sup>
ACES	$HL^+ = H^+ + L^-$ , (HL = C <sub>4</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub> S)	6.847	30.43	-49
Acetate	$HL = H^+ + L^-$ , (HL = C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> )	4.756	-0.41	-142
ADA	$H_3L^+ = H^+ + H_2L^+$ , (H <sub>2</sub> L = C <sub>6</sub> H <sub>10</sub> N <sub>2</sub> O <sub>5</sub> )	1.59		
	$H_2L^+ = H^+ + HL^+$	2.48		
	$HL^+ = H^+ + L^+$	6.844	16.7	
2-Amino-2-methyl-1,3-propanediol	$HL^+ = H^+ + L$ , (L = C <sub>4</sub> H <sub>11</sub> NO <sub>2</sub> )	8.801	49.85	-44
2-Amino-2-methyl-1-propanol	$HL^+ = H^+ + L$ , (L = C <sub>4</sub> H <sub>11</sub> NO)	9.694	54.05	≈-21
3-Amino-1-propanesulfonic acid	$HL = H^+ + L^-$ , (HL = C <sub>3</sub> H <sub>9</sub> NO <sub>3</sub> S)	10.2		
Ammonia	$NH_4^+ = H^+ + NH_3$	9.245	51.95	8
AMPSO	$HL^+ = H^+ + L^-$ , (HL = C <sub>7</sub> H <sub>17</sub> NO <sub>5</sub> S)	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 <sub>2</sub> L = C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> )	7.980	24.27	-135
	$HL^- = H^+ + L^{2-}$	12.8		
BES	$HL^+ = H^+ + L^-$ , (HL = C <sub>6</sub> H <sub>15</sub> NO <sub>5</sub> S)	7.187	24.25	-2
Bicine	$H_2L^+ = H^+ + HL^+$ , (HL = C <sub>6</sub> H <sub>13</sub> NO <sub>4</sub> )	2.0		
	$HL^+ = H^+ + L^-$	8.334	26.34	0
Bis-tris	$H_3L^+ = H^+ + H_2L^+$ , (H <sub>2</sub> L = C <sub>8</sub> H <sub>19</sub> NO <sub>5</sub> )	6.484	28.4	27
Bis-tris propane	$H_2L^{2+} = H^+ + HL^+$ , (L = C <sub>11</sub> H <sub>26</sub> N <sub>2</sub> O <sub>6</sub> )	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 <sub>2</sub> H <sub>6</sub> AsO <sub>2</sub> )	1.78	-3.5	
	$HL = H^+ + L^-$	6.28	-3.0	-86
CAPS	$HL^+ = H^+ + L^-$ , (HL = C <sub>9</sub> H <sub>19</sub> NO <sub>3</sub> S)	10.499	48.1	57
CAPSO	$HL^+ = H^+ + L^-$ , (HL = C <sub>9</sub> H <sub>19</sub> NO <sub>4</sub> S)	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	$HL^+ = H^+ + L^-$ , (HL = C <sub>8</sub> H <sub>17</sub> NO <sub>3</sub> S)	9.394	39.55	9

Buffer	Reaction	pK	$\Delta_r H^\circ$	$\Delta_r C_p^\circ$
			kJ mol <sup>-1</sup>	J K <sup>-1</sup> mol <sup>-1</sup>
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 <sub>4</sub>	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 <sub>5</sub>	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 <sub>1</sub>	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	pK	$\Delta_r H^\circ$	$\Delta_r C_p^\circ$
			kJ mol <sup>-1</sup>	J K <sup>-1</sup> mol <sup>-1</sup>
Sulfite	$\text{H}_2\text{SO}_3 = \text{H}^+ + \text{HSO}_3^-$	1.857	-17.80	-272
	$\text{HSO}_3^- = \text{H}^+ + \text{SO}_3^{2-}$	7.172	-3.65	-262
TAPS	$\text{HL}^\pm = \text{H}^+ + \text{L}^-$ , (HL = C <sub>7</sub> H <sub>17</sub> NO <sub>6</sub> S)	8.44	40.4	15
TAPSO	$\text{HL}^\pm = \text{H}^+ + \text{L}^-$ , (HL = C <sub>7</sub> H <sub>17</sub> NO <sub>7</sub> S)	7.635	39.09	-16
L(+)-Tartaric acid	$\text{H}_2\text{L} = \text{H}^+ + \text{HL}^-$ , (H <sub>2</sub> L = C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> )	3.036	3.19	-147
	$\text{HL}^- = \text{H}^+ + \text{L}^{2-}$	4.366	0.93	-218
TES	$\text{HL}^\pm = \text{H}^+ + \text{L}^-$ , (HL = C <sub>6</sub> H <sub>15</sub> NO <sub>6</sub> S)	7.550	32.13	0
Tricine	$\text{H}_2\text{L}^+ = \text{H}^+ + \text{HL}^\pm$ , (HL = C <sub>6</sub> H <sub>13</sub> NO <sub>2</sub> )	2.023	5.85	-196
	$\text{HL}^\pm = \text{H}^+ + \text{L}^-$	8.135	31.37	-53
Triethanolamine	$\text{HL}^+ = \text{H}^+ + \text{L}$ , (L = C <sub>6</sub> H <sub>15</sub> NO <sub>3</sub> )	7.762	33.6	50
Triethylamine	$\text{HL}^+ = \text{H}^+ + \text{L}$ , (L = C <sub>6</sub> H <sub>15</sub> N)	10.72	43.13	151
Tris	$\text{HL}^+ = \text{H}^+ + \text{L}$ , (L = C <sub>4</sub> H <sub>11</sub> NO <sub>3</sub> )	8.072	47.45	-59