THERMODYNAMIC QUANTITIES FOR THE IONIZATION REACTIONS OF BUFFERS IN WATER

Robert N. Goldberg, Nand Kishore, and Rebecca M. Lennen

This table contains selected values for the pK, standard molar enthalpy of reaction $\Delta H^o$, and standard molar heat-capacity change $\Delta C^o_p$ 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 pK and of $\Delta H^o$ at temperatures in the vicinity ($T = (274$ K to 350 K) of the reference temperature $\theta = 298.15$ K by using the following equations $^2$:

$$\Delta G^o_T = -RT \ln K_T = \ln(10)RTpK_T,$$  

(1)

$$R \ln K_T = -\frac{(\Delta G^o/\theta) + \Delta H^o/\theta \cdot (1/\theta - 1/T) + \Delta C^o_p/\theta \cdot (T/\theta - 1 + \ln(T/\theta))}{(\theta/\theta - 1 + \ln(T/\theta))},$$  

(2)

$$\Delta H^o_T = \Delta H^o/\theta + \Delta C^o_p(\theta - T).$$  

(3)

Here, $\Delta G^o$ 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 pK as a function of temperature:

$$pK_T = -\frac{[\ln(10)RTpK_T]}{-\frac{[\ln(10)RTpK_T]}{\theta} + \Delta H^o/\theta \cdot (1/\theta - 1/T) + \Delta C^o_p(\theta - T)}.$$  

(4)

The above equations neglect higher order terms that involve temperature derivatives of $\Delta C^o_p$. Also, it is important to recognize that the values of pK and $\Delta H^o$ effectively pertain to ionic strength $I = 0$. However, the values of pK and $\Delta H^o$ 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.


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

<table>
<thead>
<tr>
<th>Buffer</th>
<th>Reaction</th>
<th>pK</th>
<th>$\Delta H^o$</th>
<th>$\Delta C^o_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACES</td>
<td>$H^+ + L_\text{H} = H^+ + L^-$ (HL = C$<em>8$H$</em>{10}$N$_2$O$_4$S)</td>
<td>6.847</td>
<td>30.43</td>
<td>49</td>
</tr>
<tr>
<td>Acetate</td>
<td>$H^+ + L_\text{H} = H^+ + L^-$ (HL = C$_2$H$_4$O$_2$)</td>
<td>4.756</td>
<td>0.41</td>
<td>142</td>
</tr>
<tr>
<td>ADA</td>
<td>$H^+ + L_\text{H} = H^+ + L^-$ (HL = C$<em>6$H$</em>{10}$N$_2$O$_5$)</td>
<td>1.59</td>
<td>16.7</td>
<td>144</td>
</tr>
<tr>
<td>2-Amino-2-methyl-1,3-propanediol</td>
<td>$H^+ + L_\text{L} = H^+ + L^-$ (HL = C$<em>8$H$</em>{10}$N$_2$O$_5$S)</td>
<td>1.59</td>
<td>16.7</td>
<td>144</td>
</tr>
<tr>
<td>2-Amino-2-methyl-1-propanol</td>
<td>$H^+ + L_\text{L} = H^+ + L^-$ (HL = C$_4$H$_9$NO)</td>
<td>9.694</td>
<td>54.05</td>
<td>21</td>
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<tr>
<td>3-Amino-1-propanesulfonic acid</td>
<td>$H^+ + L_\text{H} = H^+ + L^-$ (HL = C$<em>8$H$</em>{10}$N$_2$O$_5$S)</td>
<td>10.2</td>
<td>54.05</td>
<td>21</td>
</tr>
<tr>
<td>Ammonia</td>
<td>$H^+ + NH_4$</td>
<td>9.245</td>
<td>51.95</td>
<td>8</td>
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<tr>
<td>AMPSO</td>
<td>$H^+ + L_\text{H} = H^+ + L^-$ (HL = C$_2$H$_4$O$_2$)</td>
<td>9.138</td>
<td>43.19</td>
<td>61</td>
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<tr>
<td>Arsenate</td>
<td>$H^+ + L_\text{H} = H^+ + L^-$ (HL = C$_2$H$_4$O$_2$)</td>
<td>1.7</td>
<td>7.8</td>
<td>61</td>
</tr>
<tr>
<td>Barbital</td>
<td>$H^+ + L_\text{H} = H^+ + L^-$ (HL = C$<em>8$H$</em>{10}$N$_2$O$_5$S)</td>
<td>7.980</td>
<td>24.27</td>
<td>135</td>
</tr>
<tr>
<td>BES</td>
<td>$H^+ + L_\text{H} = H^+ + L^-$ (HL = C$_2$H$_4$O$_2$)</td>
<td>7.834</td>
<td>26.34</td>
<td>0</td>
</tr>
<tr>
<td>Bicine</td>
<td>$H^+ + L_\text{H} = H^+ + L^-$ (HL = C$_2$H$_4$O$_2$)</td>
<td>6.484</td>
<td>28.4</td>
<td>27</td>
</tr>
<tr>
<td>Bis-tris</td>
<td>$H^+ + L_\text{H} = H^+ + L^-$ (HL = C$<em>8$H$</em>{10}$N$_2$O$_5$S)</td>
<td>6.65</td>
<td>28.4</td>
<td>27</td>
</tr>
<tr>
<td>Bis-tris propane</td>
<td>$H^+ + L_\text{H} = H^+ + L^-$ (HL = C$<em>8$H$</em>{10}$N$_2$O$_5$S)</td>
<td>9.10</td>
<td>24.27</td>
<td>135</td>
</tr>
<tr>
<td>Borate</td>
<td>$H^+ + L_\text{H} = H^+ + L^-$ (HL = C$_2$H$_4$O$_2$)</td>
<td>9.237</td>
<td>13.8</td>
<td>240</td>
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<tr>
<td>Cacodylate</td>
<td>$H^+ + L_\text{H} = H^+ + L^-$ (HL = C$_2$H$_4$O$_2$)</td>
<td>9.237</td>
<td>13.8</td>
<td>240</td>
</tr>
<tr>
<td>CAPS</td>
<td>$H^+ + L_\text{H} = H^+ + L^-$ (HL = C$_2$H$_4$O$_2$)</td>
<td>10.499</td>
<td>48.1</td>
<td>57</td>
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<tr>
<td>CAPSO</td>
<td>$H^+ + L_\text{H} = H^+ + L^-$ (HL = C$_2$H$_4$O$_2$)</td>
<td>9.825</td>
<td>46.67</td>
<td>21</td>
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<tr>
<td>Carbonate</td>
<td>$H^+ + L_\text{H} = H^+ + L^-$ (HL = C$_2$H$_4$O$_2$)</td>
<td>6.351</td>
<td>9.15</td>
<td>371</td>
</tr>
<tr>
<td>CHES</td>
<td>$H^+ + L_\text{H} = H^+ + L^-$ (HL = C$<em>8$H$</em>{10}$N$_2$O$_5$S)</td>
<td>9.394</td>
<td>39.55</td>
<td>9</td>
</tr>
<tr>
<td>Buffer</td>
<td>Reaction</td>
<td>pK</td>
<td>$\Delta H$</td>
<td>$\Delta C_p$</td>
</tr>
<tr>
<td>------------------</td>
<td>-----------------------------------------------</td>
<td>------</td>
<td>------------</td>
<td>--------------</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>kJ mol⁻¹</td>
<td>J mol⁻¹ K⁻¹</td>
</tr>
<tr>
<td>Citrate</td>
<td>$H_3L = H^+ + H_2L^-$, $(H_2L = C_6H_8O_7)$</td>
<td>3.128</td>
<td>4.07</td>
<td>−131</td>
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<tr>
<td></td>
<td>$H_2L^+ = H^+ + L^-$</td>
<td>4.761</td>
<td>2.23</td>
<td>−178</td>
</tr>
<tr>
<td></td>
<td>$H_2L = H^+ + L^-$</td>
<td>6.396</td>
<td>−3.38</td>
<td>−254</td>
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<tr>
<td>t-Cysteine</td>
<td>$H_2L = H^+ + HCl$, $(H_2L = C_2H_5NO_3S)$</td>
<td>1.71</td>
<td>−0.6</td>
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<tr>
<td></td>
<td>$H_2L = H^+ + L^-$</td>
<td>8.36</td>
<td>36.1</td>
<td>−66</td>
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<tr>
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<td>$H_2L = H^+ + L^-$</td>
<td>10.75</td>
<td>34.1</td>
<td>−204</td>
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<tr>
<td>Diethanolamine</td>
<td>$H_2L = H^+ + L^-$, $(L = C_2H_5NO)$</td>
<td>8.883</td>
<td>42.08</td>
<td>36</td>
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<tr>
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<td>$H_2L = H^+ + L^-$</td>
<td>3.05</td>
<td>−0.1</td>
<td>−142</td>
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<tr>
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<td>$H_2L = H^+ + L^-$</td>
<td>4.37</td>
<td>−7.2</td>
<td>−138</td>
</tr>
<tr>
<td>3,3-Dimethylglutarate</td>
<td>$H_3L = H^+ + H_2L$, $(H_2L = C_6H_{12}O_4)$</td>
<td>3.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$H_2L = H^+ + L^-$</td>
<td>6.34</td>
<td></td>
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<tr>
<td></td>
<td>$H_2L = H^+ + L^-$</td>
<td>6.65</td>
<td>−1.85</td>
<td>−212</td>
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<td>$H_2L = H^+ + L^-$</td>
<td>9.78</td>
<td>44.2</td>
<td>−57</td>
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<tr>
<td>Glycine amide</td>
<td>$H_2L = H^+ + L^-$, $(L = C_2H_5NO)$</td>
<td>8.04</td>
<td>42.9</td>
<td></td>
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<tr>
<td></td>
<td>$H_2L = H^+ + L^-$</td>
<td>1.34</td>
<td>0.11</td>
<td>−128</td>
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<tr>
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<td>$H_2L = H^+ + L^-$</td>
<td>8.26</td>
<td>43.4</td>
<td>−16</td>
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<tr>
<td>Glycylglycine</td>
<td>$H_2L = H^+ + L^-$, $(H_2L = C_2H_5NO_2)$</td>
<td>3.22</td>
<td>0.84</td>
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<tr>
<td></td>
<td>$H_2L = H^+ + L^-$</td>
<td>8.09</td>
<td>41.7</td>
<td></td>
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<tr>
<td>HEPES</td>
<td>$H_2L = H^+ + L^-$, $(H_2L = C_6H_{12}N_4O_3S)$</td>
<td>≈3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$H_2L = H^+ + L^-$</td>
<td>7.56</td>
<td>20.4</td>
<td>47</td>
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<tr>
<td></td>
<td>$H_2L = H^+ + L^-$</td>
<td>7.95</td>
<td>21.3</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>$H_2L = H^+ + L^-$</td>
<td>8.04</td>
<td>23.7</td>
<td>47</td>
</tr>
<tr>
<td>1-Histidine</td>
<td>$H_2L = H^+ + L^-$, $(H_2L = C_6H_{12}N_4O_3)$</td>
<td>1.5</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$H_2L = H^+ + L^-$</td>
<td>6.07</td>
<td>29.5</td>
<td>176</td>
</tr>
<tr>
<td></td>
<td>$H_2L = H^+ + L^-$</td>
<td>9.34</td>
<td>43.8</td>
<td>−233</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>$H_2L = H^+ + L^-$, $(L = C_2H_5N)$</td>
<td>−0.99</td>
<td>38.1</td>
<td></td>
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<tr>
<td></td>
<td>$H_2L = H^+ + L^-$</td>
<td>8.02</td>
<td>41.7</td>
<td></td>
</tr>
<tr>
<td>Imidazole</td>
<td>$H_2L = H^+ + L^-$, $(L = C_2H_5N)$</td>
<td>6.99</td>
<td>36.6</td>
<td>−9</td>
</tr>
<tr>
<td>Maleate</td>
<td>$H_2L = H^+ + L^-$, $(H_2L = C_2H_5NO)$</td>
<td>1.92</td>
<td>1.1</td>
<td>−21</td>
</tr>
<tr>
<td></td>
<td>$H_2L = H^+ + L^-$</td>
<td>6.27</td>
<td>−3.6</td>
<td>−31</td>
</tr>
<tr>
<td>2-Mercaptoethanol</td>
<td>$H_2L = H^+ + L^-$, $(H_2L = C_2H_6O_2S)$</td>
<td>9.7</td>
<td>26.2</td>
<td></td>
</tr>
<tr>
<td>MES</td>
<td>$H_2L = H^+ + L^-$, $(H_2L = C_2H_5NO)$</td>
<td>6.27</td>
<td>14.8</td>
<td>5</td>
</tr>
<tr>
<td>Methylamine</td>
<td>$H_2L = H^+ + L^-$, $(L = CH_5N)$</td>
<td>10.65</td>
<td>55.3</td>
<td>33</td>
</tr>
<tr>
<td>2-Methylimidazole</td>
<td>$H_2L = H^+ + L^-$, $(L = C_2H_5N)$</td>
<td>8.0</td>
<td>36.8</td>
<td></td>
</tr>
<tr>
<td>MOPS</td>
<td>$H_2L = H^+ + L^-$, $(H_2L = C_2H_5NO)$</td>
<td>7.18</td>
<td>21.1</td>
<td>25</td>
</tr>
<tr>
<td>MOPSO</td>
<td>$H_2L = H^+ + L^-$, $(H_2L = C_2H_5NO)$</td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OXALATE</td>
<td>$H_2L = H^+ + L^-$, $(H_2L = C_2H_4O_2)$</td>
<td>1.27</td>
<td>−3.9</td>
<td>−231</td>
</tr>
<tr>
<td></td>
<td>$H_2L = H^+ + L^-$</td>
<td>4.266</td>
<td>7.00</td>
<td>−231</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>$H_2PO_4^− = H^+ + HPO_4^−$</td>
<td>2.148</td>
<td>−8.0</td>
<td>−141</td>
</tr>
<tr>
<td></td>
<td>$H_2PO_4^− = H^+ + HPO_4^−$</td>
<td>7.198</td>
<td>3.6</td>
<td>−230</td>
</tr>
<tr>
<td></td>
<td>$H_2PO_4^− = H^+ + PO_4^−$</td>
<td>12.35</td>
<td>16.0</td>
<td>−242</td>
</tr>
<tr>
<td>Phthalate</td>
<td>$H_2L = H^+ + L^-$, $(H_2L = C_2H_4O_2)$</td>
<td>2.95</td>
<td>−2.70</td>
<td>−91</td>
</tr>
<tr>
<td></td>
<td>$H_2L = H^+ + L^-$</td>
<td>5.408</td>
<td>−2.17</td>
<td>−295</td>
</tr>
<tr>
<td>Piperazine</td>
<td>$H_2L = H^+ + L^-$, $(L = C_2H_5N_2)$</td>
<td>5.33</td>
<td>31.1</td>
<td>86</td>
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<tr>
<td></td>
<td>$H_2L = H^+ + L^-$</td>
<td>9.73</td>
<td>42.89</td>
<td>75</td>
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<tr>
<td>PIPES</td>
<td>$H_2L = H^+ + L^-$, $(H_2L = C_2H_5NO_2S)$</td>
<td>7.14</td>
<td>11.2</td>
<td>22</td>
</tr>
<tr>
<td>POPOSO</td>
<td>$H_2L = H^+ + L^-$, $(H_2L = C_2H_5NO_2S)$</td>
<td>≈8.0</td>
<td></td>
<td></td>
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<tr>
<td>Pyrophosphate</td>
<td>$H_3P_2O_6 = H^+ + H_3PO_4$</td>
<td>0.83</td>
<td>−9.2</td>
<td>−90</td>
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<td></td>
<td>$H_3P_2O_6 = H^+ + H_2PO_4^−$</td>
<td>2.26</td>
<td>−5.0</td>
<td>−130</td>
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<td></td>
<td>$H_3P_2O_6 = H^+ + HP_2O_4^−$</td>
<td>6.72</td>
<td>0.5</td>
<td>−136</td>
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<tr>
<td></td>
<td>$H_3P_2O_6 = H^+ + PO_4^−$</td>
<td>9.46</td>
<td>1.4</td>
<td>−141</td>
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<tr>
<td>Succinate</td>
<td>$H_2L = H^+ + L^-$, $(H_2L = C_2H_4O_2)$</td>
<td>4.207</td>
<td>3.0</td>
<td>−121</td>
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<tr>
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<td>$H_2L = H^+ + L^-$</td>
<td>5.63</td>
<td>−0.5</td>
<td>−217</td>
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<tr>
<td>Sulfate</td>
<td>$H_2SO_4 = H^+ + SO_4^−$</td>
<td>1.987</td>
<td>−22.4</td>
<td>−258</td>
</tr>
<tr>
<td>Buffer</td>
<td>Reaction</td>
<td>pK</td>
<td>$\Delta H^\circ$</td>
<td>$\Delta C_p^\circ$</td>
</tr>
<tr>
<td>-------------------</td>
<td>-----------------------------------------------</td>
<td>------</td>
<td>-------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Sulfite</td>
<td>$H_2SO_3 = H^+ + HSO_3^-$</td>
<td>1.857</td>
<td>$-17.80$</td>
<td>$-272$</td>
</tr>
<tr>
<td></td>
<td>$HSO_3^- = H^+ + SO_4^{2-}$</td>
<td>7.172</td>
<td>$-3.65$</td>
<td>$-262$</td>
</tr>
<tr>
<td>TAPS</td>
<td>$HL^+ = H^+ + L^-$, (HL = C$<em>7$H$</em>{17}$NO$_5$S)</td>
<td>8.44</td>
<td>40.4</td>
<td>15.0</td>
</tr>
<tr>
<td>TAPSO</td>
<td>$HL^+ = H^+ + L^-$, (HL = C$<em>7$H$</em>{17}$NO$_5$S)</td>
<td>7.635</td>
<td>39.09</td>
<td>-16.0</td>
</tr>
<tr>
<td>l(+)-Tartaric acid</td>
<td>$H_2L = H^+ + HL^-$, (H$_2L = C_4$H$_6$O$_6$)</td>
<td>3.036</td>
<td>3.19</td>
<td>-147.0</td>
</tr>
<tr>
<td></td>
<td>$HL^- = H^+ + L^{2-}$</td>
<td>4.366</td>
<td>0.93</td>
<td>-218.0</td>
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<tr>
<td>TES</td>
<td>$HL^+ = H^+ + L^-$, (HL = C$<em>6$H$</em>{15}$NO$_6$S)</td>
<td>7.550</td>
<td>32.13</td>
<td>0.0</td>
</tr>
<tr>
<td>Tricine</td>
<td>$H_2L^+ = H^+ + HL^+$, (HL = C$<em>6$H$</em>{15}$NO$_6$)</td>
<td>2.023</td>
<td>5.85</td>
<td>-196.0</td>
</tr>
<tr>
<td></td>
<td>$HL^+ = H^+ + L^-$</td>
<td>8.135</td>
<td>31.37</td>
<td>-53.0</td>
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<tr>
<td>Triethanolamine</td>
<td>$HL^+ = H^+ + L^-$, (L = C$<em>6$H$</em>{15}$NO$_3$)</td>
<td>7.762</td>
<td>33.6</td>
<td>50.0</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>$HL^+ = H^+ + L^-$, (L = C$<em>6$H$</em>{15}$N)</td>
<td>10.72</td>
<td>43.13</td>
<td>151.0</td>
</tr>
<tr>
<td>Tris</td>
<td>$HL^+ = H^+ + L^-$, (L = C$<em>6$H$</em>{11}$NO$_2$)</td>
<td>8.072</td>
<td>47.45</td>
<td>-59.0</td>
</tr>
</tbody>
</table>