

# Group Contribution Values of the Infinite Dilution Thermodynamic Functions of Hydration for Aliphatic Noncyclic Hydrocarbons, Alcohols, and Ketones at 298.15 K and 0.1 MPa<sup>†</sup>

Andrey V. Plyasunov\* and Everett L. Shock

Group Exploring Organic Processes in Geochemistry (GEOPIG), Department of Earth and Planetary Sciences, Washington University, St. Louis, Missouri 63130

A compilation of experimental values of the infinite dilution partial molar Gibbs energy, enthalpy, and heat capacity of hydration, together with molar volumes in water at 298.15 K and 0.1 MPa, is presented for aliphatic noncyclic ketones. These data, combined with the related results for aliphatic noncyclic hydrocarbons and monohydric alcohols, were treated in the framework of a simple first-order group additivity scheme. Numerical values of the contributions to each of the thermodynamic properties are obtained by the least-squares procedure for the following groups: CH<sub>3</sub>, CH<sub>2</sub>, CH, C, OH, and CO.

## Introduction

Values of thermodynamic properties of organic compounds in aqueous solutions at infinite dilution are needed for many applications in chemistry, biology, medicine, geochemistry, chemical engineering, and so forth. An experimental study of all the variety of organic compounds is out of the question: there are simply too many substances to make a comprehensive study possible. Instead, group additivity methods have been used to estimate the properties of organic species in gas, liquid, and solid phases (see refs 1–3). In 1981, Cabani et al.<sup>4</sup> presented an extensive database of thermodynamic functions of hydration of organic compounds at 298.15 K and derived group contribution values for many functional groups. Recently, attempts<sup>5</sup> have been made to update the database and group contribution values for aliphatic and monoaromatic hydrocarbons and monohydric alcohols. Here we present the results for aliphatic noncyclic ketones.

## Data Compilation

The infinite dilution partial molar functions of hydration under consideration are the Gibbs energy,  $\Delta_{\text{h}}G^{\circ}$ , the enthalpy,  $\Delta_{\text{h}}H^{\circ}$ , the heat capacity,  $\Delta_{\text{h}}C_p^{\circ}$ , and the volume,  $V_2$ . The standard state adopted for gaseous species is unit fugacity of the ideal gas at any temperature and pressure  $P^{\circ} = 0.1$  MPa; that for aqueous species calls for unit activity of a hypothetical 1 *m* solution referenced to infinite dilution at any temperature and pressure. The hydration process refers to transfer of 1 mol of a solute from an ideal gas to a standard 1 *m* solution. We note two main reasons to work with the functions of hydration rather than with the partial molar properties, like the Gibbs energy of formation of an aqueous compound. First, functions of hydration typically have lower uncertainties, because they do not include the uncertainties of the enthalpy of combustion measurements. Second, as discussed by Cabani et al.,<sup>4</sup> there is a universal contribution to the properties of

aqueous species, which is seen as the nonzero intercept of a plot of properties for a homologous series versus molecular mass or number of groups. The nature of this term is obvious for the thermodynamic functions of hydration, where it arises as the functions of hydration of a material point.<sup>6</sup> This term can be calculated independently using the thermophysical properties of pure water, thus reducing the dimension of the fitting task.

**Gibbs Energy of Hydration at 298.15 K.** Literature values of the various modifications of Henry's law constants and gas/water partition coefficients were recalculated to yield equilibrium constants,  $K^{\circ}$ , for a gas dissolution reaction  $A(\text{g}) \rightleftharpoons A(\text{aq})$ , for which  $\Delta_{\text{h}}G^{\circ} = -RT \ln K^{\circ} = -RT \ln(aP^{\circ}/f)$ , where *a* and *f* stand for the activity and fugacity, respectively, of a solute in water, and  $P^{\circ}$  is the ideal gas standard state pressure.

Results for the infinite dilution activity coefficient of a solute for the symmetrical normalization of activities, reported as  $\gamma^{\infty}$  were converted to  $\Delta_{\text{h}}G^{\circ}$  values as follows (see ref 5):  $\Delta_{\text{h}}G^{\circ} = -\Delta_{\text{vap}}G^{\circ} + RT \ln \gamma^{\infty} - RT \ln 1000/M_w$ , where  $M_w$  stands for the molecular mass of water in grams per mole;  $\Delta_{\text{vap}}G^{\circ} = -RT \ln(\psi P_s/P^{\circ})$ , where  $P_s$  stands for the saturated vapor pressure over the pure liquid/solid compound and  $\psi$  represents the fugacity coefficient of a pure compound, evaluated using the second virial coefficient.

The mutual solubility data were converted to  $\Delta_{\text{h}}G^{\circ}$  values as follows (see ref 5):  $\Delta_{\text{h}}G^{\circ} = \Delta_{\text{sol}}G^{\circ} - \Delta_{\text{vap}}G^{\circ}$ , where  $\Delta_{\text{sol}}G^{\circ} = -RT \ln(m_s \gamma_{m,s} / X_s \gamma_{x,s})$ , where  $m_s$  and  $\gamma_{m,s}$  stand for the molality and the molal activity coefficient (for the unsymmetrical normalization) at saturation for an organic compound in the water-rich phase, respectively;  $X_s$  and  $\gamma_{x,s}$  represent the mole fraction and the mole fraction activity coefficient (for the symmetrical normalization) of the organic compound in the coexisting organic-rich phase. The UNIQUAC model<sup>7</sup> was employed to evaluate  $\gamma_{x,s}$ . Values of  $\gamma_{m,s}$  were estimated using the Savage and Wood<sup>8</sup> group contribution scheme. In the Savage–Wood formalism,  $\ln \gamma_{m,s} = 2g_{xx}m_s/RT$ , where  $g_{xx}$  is the solute–solute self-interaction coefficient, given by  $g_{xx} = \sum_{i,j} n_i n_j G_{ij} - RTM_w/2000$ , where  $n_i$  and  $n_j$  represent the number of groups *i* and *j* in two interacting molecules and  $G_{ij}$  stands for the excess Gibbs energy of an *i*–*j* interaction. To characterize the ketone–ketone interactions, one needs  $G_{\text{CH}_2-\text{CH}_2} = -34$

<sup>†</sup> This contribution will be part of a special print edition containing papers presented at the Fourteenth Symposium on Thermophysical Properties, Boulder, CO, June 25–30, 2000.

\* Corresponding author. Fax: (314)-935-7361. Phone: (314)-935-7435. E-mail: andrey@zonvark.wustl.edu.

**Table 1. Values of the Gibbs Energies of Hydration of Ketones at 298.15 K and 0.1 MPa (See Text for Details)**

compound	formula	$\Delta_{\text{vap}}G^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{vap}}G^\circ/\text{kJ}\cdot\text{mol}^{-1}$	accepted value	group contribution value	$\Delta/\text{kJ}\cdot\text{mol}^{-1}$
acetone	C <sub>3</sub> H <sub>6</sub> O	2.987, <sup>a</sup>	-7.89, <sup>12</sup> -8.21, <sup>13</sup> -8.14, <sup>14</sup> -8.59, <sup>15</sup> -8.01, <sup>16</sup> -8.79, <sup>17</sup> -8.02, <sup>18</sup> -8.02, <sup>19</sup> -7.93, <sup>20</sup> -7.94, <sup>21</sup> -8.00, <sup>22</sup> -8.22, <sup>23</sup> -8.29, <sup>24</sup> -8.43 <sup>25</sup>	-8.18 ± 0.30	-7.48	-0.70
2-butanone	C <sub>4</sub> H <sub>8</sub> O	5.287, <sup>a</sup>	(-8.75), <sup>12</sup> -7.18, <sup>11</sup> -7.01, <sup>16</sup> -7.40, <sup>17</sup> (-5.06), <sup>26</sup> -7.11, <sup>27</sup> -6.97, <sup>28</sup> -6.97, <sup>29</sup> (-5.87), <sup>19</sup> -6.99, <sup>20</sup> -7.28, <sup>30</sup> -7.41, <sup>31</sup> -7.13, <sup>21</sup> -7.58 <sup>22</sup>	-7.18 ± 0.30	-6.76	-0.42
2-pentanone	C <sub>5</sub> H <sub>10</sub> O	7.607, <sup>a</sup>	-6.12, <sup>32</sup> -6.34, <sup>33</sup> -6.19, <sup>34</sup> -6.09, <sup>16</sup> -6.17, <sup>35</sup> -6.14, <sup>20</sup> -6.42, <sup>30</sup> -6.52, <sup>31</sup> -6.21, <sup>36</sup> -6.80, <sup>22</sup> -5.96 <sup>37</sup>	-6.27 ± 0.40	-6.05	-0.22
3-pentanone	C <sub>5</sub> H <sub>10</sub> O	7.597, <sup>a</sup>	-5.82, <sup>34</sup> -5.83, <sup>16</sup> -5.81, <sup>20</sup> -6.76, <sup>31</sup> -5.81 <sup>36</sup>	-6.01 ± 0.40	-6.05	0.04
3-methyl-2-butanone	C <sub>5</sub> H <sub>10</sub> O	6.637, <sup>a</sup>	-5.42, <sup>34</sup> -5.61, <sup>38</sup> -5.56, <sup>35</sup> -5.29 <sup>36</sup>	-5.47 ± 0.30	-5.60	0.13
2-hexanone	C <sub>6</sub> H <sub>12</sub> O	10.35 <sup>39,a</sup>	-5.67, <sup>34</sup> -5.64, <sup>20</sup> -5.48, <sup>30</sup> -5.67, <sup>31</sup> -5.87 <sup>36</sup>	-5.67 ± 0.30	-5.34	-0.33
3-hexanone	C <sub>6</sub> H <sub>12</sub> O	9.92 <sup>39,a</sup>	(0.63), <sup>40</sup> -4.95, <sup>20</sup> -5.14 <sup>36</sup>	-5.01 ± 0.30	-5.34	0.33
4-methyl-2-pentanone	C <sub>6</sub> H <sub>12</sub> O	9.11 <sup>39,a</sup>	-4.64, <sup>41</sup> -4.81, <sup>34</sup> (-2.33), <sup>26</sup> -4.74, <sup>31</sup> -4.91 <sup>36</sup>	-4.78 ± 0.30	-4.88	0.10
2-methyl-3-pentanone	C <sub>6</sub> H <sub>12</sub> O	8.80 <sup>39,a</sup>	-4.12 <sup>36</sup>	-4.12 ± 0.60	-4.88	0.76
3-methyl-2-pentanone	C <sub>6</sub> H <sub>12</sub> O	9.24 <sup>39,a</sup>	-5.28 <sup>36</sup>	-5.28 ± 0.60	-4.88	-0.40
3,3-dimethyl-2-butanone	C <sub>6</sub> H <sub>12</sub> O	7.83 <sup>39,a</sup>	-3.68, <sup>34</sup> -3.83, <sup>30</sup> -3.63 <sup>36</sup>	-3.71 ± 0.40	-4.64	0.93
2-heptanone	C <sub>7</sub> H <sub>14</sub> O	13.04 <sup>42</sup>	-4.38, <sup>32</sup> -4.83, <sup>34</sup> -4.81, <sup>30</sup> -5.45, <sup>31</sup> -5.02, <sup>36</sup> -4.77 <sup>22</sup>	-4.88 ± 0.40	-4.63	-0.26
4-heptanone	C <sub>7</sub> H <sub>14</sub> O	12.54 <sup>39,a</sup>	-4.50 <sup>16</sup>	-4.50 ± 0.60	-4.63	0.13
2,4-dimethyl-3-pentanone	C <sub>7</sub> H <sub>14</sub> O	9.79 <sup>39,a</sup>	-1.89, <sup>34</sup> -2.37 <sup>36</sup>	-2.13 ± 0.50	-3.72	1.59
2-octanone	C <sub>8</sub> H <sub>16</sub> O	15.84 <sup>42</sup>	-4.70, <sup>34</sup> -4.28, <sup>43</sup> -4.11 <sup>22</sup>	-4.36 ± 0.40	-3.91	-0.45
2-nonanone	C <sub>9</sub> H <sub>18</sub> O	18.46 <sup>42</sup>	-3.53, <sup>44</sup> -3.76, <sup>34</sup> -2.45 <sup>22</sup>	-3.25 ± 0.50	-3.20	-0.05
2,6-dimethyl-4-heptanone	C <sub>9</sub> H <sub>18</sub> O	15.07 <sup>39,a</sup>	-0.73 <sup>34</sup>	-0.73 ± 1.00	-2.29	1.56
2-undecanone	C <sub>11</sub> H <sub>22</sub> O	24.28 <sup>39,a</sup>	-1.09, <sup>22</sup> -2.12 <sup>22</sup>	-1.6 ± 0.6	-1.78	0.18

<sup>a</sup> Value from the published compilation.

**Table 2. Values of the Enthalpy of Hydration of Ketones at 298.15 K and 0.1 MPa**

compound	formula	$\Delta_{\text{vap}}H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{h}}H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	accepted value	group contribution value	$\Delta/\text{kJ}\cdot\text{mol}^{-1}$
acetone	C <sub>3</sub> H <sub>6</sub> O	31.27 <sup>45,a</sup>	-41.70, <sup>46</sup> -41.57, <sup>47</sup> -41.44, <sup>48</sup> -41.44, <sup>49</sup> -41.24, <sup>50</sup> -41.48, <sup>51</sup> -41.18 <sup>52</sup>	-41.5 ± 0.3	-40.65	-0.85
2-butanone	C <sub>4</sub> H <sub>8</sub> O	34.92 <sup>45,a</sup>	-45.64, <sup>49</sup> -45.42 <sup>53</sup>	-45.5 ± 0.5	-44.37	-1.13
2-pentanone	C <sub>5</sub> H <sub>10</sub> O	38.46 <sup>45,a</sup>	-48.67, <sup>49</sup> -49.98 <sup>54</sup>	-49.0 ± 0.5	-48.11	-0.89
3-pentanone	C <sub>5</sub> H <sub>10</sub> O	38.68 <sup>45,a</sup>	-49.58, <sup>49</sup> -49.56 <sup>54</sup>	-49.6 ± 0.5	-48.11	-1.49
3-methyl-2-butanone	C <sub>5</sub> H <sub>10</sub> O	36.87 <sup>45,a</sup>	-47.50 <sup>49</sup>	-47.6 ± 1.0	-48.26	0.66
2-hexanone	C <sub>6</sub> H <sub>12</sub> O	43.15 <sup>45,a</sup>	-52.61 <sup>49</sup>	-52.6 ± 1.0	-51.86	-0.74
4-methyl-2-pentanone	C <sub>6</sub> H <sub>12</sub> O	40.65 <sup>45,a</sup>	-50.15 <sup>49</sup>	-50.2 ± 1.0	-52.00	1.80
3,3-dimethyl-2-butanone	C <sub>6</sub> H <sub>12</sub> O	38.00 <sup>45,a</sup>	-47.50 <sup>49</sup>	-47.5 ± 1.0	-51.34	3.84
2-heptanone	C <sub>7</sub> H <sub>14</sub> O	47.24 <sup>45,a</sup>	-56.19, <sup>49</sup> -56.86 <sup>54</sup>	-56.4 ± 0.6	-55.60	-0.80
4-heptanone	C <sub>7</sub> H <sub>14</sub> O	47.2 <sup>39,b</sup>	-58.1 <sup>54</sup>	-58.1 ± 2.0	-55.60	-2.50
2,4-dimethyl-3-pentanone	C <sub>7</sub> H <sub>14</sub> O	41.57 <sup>45,a</sup>	-51.2, <sup>49</sup> -57.1 <sup>54</sup>	-54.0 ± 3.0	-55.88	1.88
2-nonanone	C <sub>9</sub> H <sub>18</sub> O	56.44 <sup>45,a</sup>	-62.7 <sup>54</sup>	-62.7 ± 2.0	-63.08	0.38

<sup>a</sup> Recommended value from the compilation of calorimetric values of enthalpies of vaporization. <sup>b</sup> Estimated value from the temperature dependence of the saturated vapor pressure.

**Table 3. Values of the Heat Capacity of Hydration of Ketones at 298.15 K and 0.1 MPa**

compound	formula	$C_p(\text{ig})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_{\text{h}}C_p/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	accepted value	group contribution value	$\Delta/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
acetone	C <sub>3</sub> H <sub>6</sub> O	74.5 <sup>3</sup>	150, <sup>55</sup> 166 <sup>56</sup>	158 ± 10	163	-5
2-butanone	C <sub>4</sub> H <sub>8</sub> O	103.3 <sup>3</sup>	234, <sup>57</sup> 233 <sup>58</sup>	234 ± 5	230	4
3-pentanone	C <sub>5</sub> H <sub>10</sub> O	129.9 <sup>3</sup>	298 <sup>58</sup>	298 ± 10	297	1

**Table 4. Values of  $V_2^\circ$  of Ketones in Water at 298.15 K and 0.1 MPa**

compound	formula	$V_2^\circ/\text{cm}^3\cdot\text{mol}^{-1}$	accepted value	group contribution value	$\Delta/\text{cm}^3\cdot\text{mol}^{-1}$
acetone	C <sub>3</sub> H <sub>6</sub> O	66.92, <sup>59</sup> 66.8, <sup>60</sup> 66.92, <sup>61</sup> 67.0 <sup>62</sup>	66.9 ± 0.3	66.80	0.10
2-butanone	C <sub>4</sub> H <sub>8</sub> O	82.44, <sup>57</sup> 82.56, <sup>63</sup> 82.52, <sup>58</sup> 82.9, <sup>60</sup> 82.5 <sup>62</sup>	82.5 ± 0.3	82.51	-0.01
2-pentanone	C <sub>5</sub> H <sub>10</sub> O	98.0 <sup>60</sup>	98.0 ± 2.0	98.21	-0.21
3-pentanone	C <sub>5</sub> H <sub>10</sub> O	98.08 <sup>58</sup>	98.1 ± 1.0	98.21	-0.11
3-methyl-2-butanone	C <sub>5</sub> H <sub>10</sub> O	95.0 <sup>60</sup>	95.0 ± 2.0	98.41	-3.41

$\text{J}\cdot\text{mol}^{-1}$ ,<sup>9</sup>  $G_{\text{CH}_2-\text{CO}} = 41 \text{ J}\cdot\text{mol}^{-1}$ , and  $G_{\text{CO}-\text{CO}} = -64 \text{ J}\cdot\text{mol}^{-1}$ ; the two later values were evaluated from the  $g_{\text{xx}}$  values for acetone<sup>10</sup> and 2-butanone.<sup>11</sup>

The values of  $\Delta_{\text{h}}G^\circ$  obtained for ketones are presented in Table 1. Where necessary, results measured within (10–20) K from 298.15 K were recalculated to this temperature using the approximation that  $\Delta_{\text{h}}H^\circ$  is constant. Results based on mutual solubility studies are given in italics.

Values considered unreliable are given in parentheses and were excluded from consideration.

**Enthalpy and Heat Capacity of Hydration, and Partial Molar Volume at 298.15 K and 0.1 MPa.** Calorimetric values of the standard enthalpy of solution of a pure liquid ketone in water,  $\Delta_{\text{s}}H^\circ$ , were converted to  $\Delta_{\text{h}}H^\circ$  by means of  $\Delta_{\text{h}}H^\circ = \Delta_{\text{s}}H^\circ - \Delta_{\text{vap}}H^\circ$ , where  $\Delta_{\text{vap}}H^\circ$

**Table 5. Numerical Values of the Group Contributions to Each Thermodynamic Function of Hydration at 298.15 K and 0.1 MPa together with Their Uncertainties at the 0.95 Confidence Level<sup>a</sup>**

group	$\Delta_{\text{h}}G^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{h}}H^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{h}}C_{\text{p}}^{\circ}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$V_2^{\circ}/\text{cm}^3\cdot\text{mol}^{-1}$
CH <sub>3</sub>	3.62 ± 0.15 (79)	-7.55 ± 0.58 (40)	128 ± 5 (26)	25.46 ± 0.89 (30)
CH <sub>2</sub>	0.71 ± 0.07 (66)	-3.74 ± 0.29 (29)	67 ± 2 (19)	15.70 ± 0.15 (22)
CH	-1.74 ± 0.30 (43)	-0.08 ± 1.44 (13)	9 ± 11 (6)	6.15 ± 0.98 (12)
C	-4.41 ± 0.54 (12)	4.39 ± 2.30 (4)	-42 ± 15 (4)	-3.46 ± 1.85 (4)
OH	-25.34 ± 0.23 (32)	-40.47 ± 1.09 (16)	1 ± 7 (16)	12.63 ± 0.97 (20)
CO	-22.68 ± 0.31 (18)	-23.24 ± 1.25 (12)	-93 ± 11 (3)	14.76 ± 1.82 (5)
Y <sub>0</sub>	7.96	-2.29	0	1.12

<sup>a</sup> The number of compounds containing the selected groups for each of the properties is given in parentheses.

stands for the standard enthalpy of vaporization of a pure compound. Results are presented in Table 2.

Published values of the infinite dilution partial molar heat capacity of aqueous solutes,  $C_{\text{p},2}^{\circ}$ , were used to calculate  $\Delta_{\text{h}}C_{\text{p}}^{\circ}$  as follows:  $\Delta_{\text{h}}C_{\text{p}}^{\circ} = C_{\text{p},2}^{\circ} - C_{\text{p}}(\text{ig})$ , where  $C_{\text{p}}(\text{ig})$  represents the heat capacity of a compound in the ideal gas state. Results are given in Table 3.

Literature values of the infinite dilution partial molar volumes of ketones in water are presented in Table 4.

### Group Contribution Values

The values of the thermodynamic functions of hydration of ketones at 298.15 K and 0.1 MPa were combined with those for aliphatic noncyclic hydrocarbons and monohydric alcohols, which were presented elsewhere.<sup>5</sup> The first-order group additivity scheme, in which the properties of a group are assumed to be independent of the group's neighbors, was chosen to treat the data. The following groups are necessary to represent the selected compounds: CH<sub>3</sub>, CH<sub>2</sub>, CH, C, OH, and CO. Assuming the properties of the groups are additive, any thermodynamic property of interest,  $Y$ , can be estimated from  $Y = Y_0 + \sum_i n_i Y_i$ , where  $n_i$  stands for the number of times the  $i$ -th group is present in the compound,  $Y_i$  designates the contribution to the  $Y$  property of the  $i$ -th group, and  $Y_0$  represents the values of thermodynamic functions of hydration of a material point, that is, an imaginable compound without any groups at all. Values of  $Y_0$  can be calculated independently using the thermophysical properties of water (ref 6; for details see ref 5). The numerical values of the group contributions given in Table 5 were derived by a weighted least-squares fit of the selected data set.

Our results can be compared only with those of Cabani et al.,<sup>4</sup> who also determined the group contribution values for the thermodynamic functions of hydration of organic compounds. However, direct comparison of results is senseless, because of different values of the  $Y_0$  term accepted here and in ref 4 (the difference is large; for instance,  $Y_0 = 1.12 \text{ cm}^3\cdot\text{mol}^{-1}$  in our method versus  $13.41 \text{ cm}^3\cdot\text{mol}^{-1}$  for the partial molar volumes, or  $-2.29 \text{ kJ}\cdot\text{mol}^{-1}$  versus  $-13.87 \text{ kJ}\cdot\text{mol}^{-1}$  in ref 4 for the partial molar enthalpies of hydration). The latter authors treated the  $Y_0$  term as an adjustable parameter in the fit; however, we accepted it to represent the thermodynamic functions of hydration of a material point. In defense of our position, there is greater theoretical clarity in our decision to choose a material point as a limiting case of a compound without any groups at all. In addition, our experience shows that fixing  $Y_0$  at its theoretical value results in a relatively small sacrifice in the goodness of the fit.<sup>5</sup> Besides, the potential extension of group contribution methods to other temperatures, where experimental data are not as extensive as at 298 K, will be easier to implement with the independently known value of  $Y_0$ . Of course, the different values of  $Y_0$  will translate into different values of the group contributions

even when the identical database is used to derive them. As every group contribution method has to reproduce data for the hydrocarbon backbone, then the effect of the  $Y_0$  variations is larger for values of CH<sub>3</sub>, CH<sub>2</sub>, CH, and C groups and smaller for the values of functional groups, like CO and OH. Indeed, the value of the Gibbs energy of hydration for the CO group obtained here,  $-22.68 \pm 0.31 \text{ kJ}\cdot\text{mol}^{-1}$ , is close to  $-23.06 \text{ kJ}\cdot\text{mol}^{-1}$ , given by Cabani et al.,<sup>4</sup> however, these values should not be compared directly, for reasons discussed above. An essential feature of this work is a comprehensive update of the database for the thermodynamic functions of hydration for ketones (see Tables 1–4), which may be valuable for many applications besides the determination of the group contribution values.

### Literature Cited

- (1) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. Additivity rules for the estimation of thermochemical properties. *Chem. Rev.* **1969**, *69*, 279–324.
- (2) Domalski, E. S.; Hearing, E. D. Estimation of the thermodynamic properties of C–H–N–O–S–halogen compounds at 298.15 K. *J. Phys. Chem. Ref. Data* **1993**, *22*, 805–1159.
- (3) Frenkel, M.; Marsh, K. N.; Wilhoit, R. C.; Kabo, G. I.; Roganov, G. N. *Thermodynamics of Organic Compounds in the Gas State*; Thermodynamics Research Center: Texas A&M University System, College Station, TX, 1994.
- (4) Cabani, S.; Gianni, P.; Mollica, V.; Lepori, L. Group contributions to the thermodynamic properties of nonionic organic solutes in dilute aqueous solution. *J. Solution Chem.* **1981**, *10*, 563–595.
- (5) Plyasunov, A. V.; Shock, E. L. Thermodynamic functions of hydration of hydrocarbons at 298.15 K and 0.1 MPa. *Geochim. Cosmochim. Acta* **2000**, *64*, 439–468.
- (6) Pierotti, R. A. A scaled particle theory of aqueous and nonaqueous solutions. *Chem. Rev.* **1976**, *76*, 717–726.
- (7) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases & Liquids*; McGraw-Hill: New York, 1987.
- (8) Savage, J. J.; Wood, R. H. Enthalpy of dilution of aqueous mixtures of amides, sugars, urea, ethylene glycol, and pentaerythritol at 25 °C: enthalpy of interaction of the hydrocarbon, amide, and hydroxyl functional groups in dilute aqueous solutions. *J. Solution Chem.* **1976**, *5*, 733–750.
- (9) Suri, S. K.; Spitzer, J. J.; Wood, R. H.; Abel, E. G.; Thompson, P. T. Interactions in aqueous nonelectrolyte systems. Gibbs energy of interaction of the ether group with the hydroxyl group and the amide group. *J. Solution Chem.* **1985**, *14*, 781–794.
- (10) Kozak, J. J.; Knight, W. S.; Kauzmann, W. Solute–solute interactions in aqueous solutions. *J. Chem. Phys.* **1968**, *48*, 675–690.
- (11) Wong, T. Y. H.; Wong-Moon, K. C.; Beach, L. J.; Chuang, Y.-F.; Koga, Y. Excess partial molar free energies, enthalpies, and entropies of 2–butanone–H<sub>2</sub>O mixtures: solute–solute interactions. *J. Phys. Chem.* **1992**, *96*, 10025–10029.
- (12) Iraci, L. T.; Baker, B. M.; Tyndall, G. S.; Orlando, J. J. Measurement of the Henry's law coefficients of 2-methyl-3-buten-2-ol, methacrolein, and methylvinyl ketone. *J. Atmos. Chem.* **1999**, *33*, 321–330.
- (13) Benkelberg, H.-J.; Hamm, S.; Warneck, P. Henry's law coefficients for aqueous solutions of acetone, acetaldehyde and acetonitrile, and equilibrium constants for the addition compounds of acetone and acetaldehyde with bisulfite. *J. Atmos. Chem.* **1995**, *20*, 17–34.
- (14) Hoff, J. T.; Mackay, D.; Cillham, R.; Shiu, W. Y. Partitioning of organic chemicals at the air–water interface in environmental systems. *Environ. Sci. Technol.* **1993**, *27*, 2174–2180.
- (15) Betterton, E. A. The partitioning of ketones between the gas and aqueous phases. *Atmos. Environ.* **1991**, *25A*, 1473–1477.

- (16) Landau, I.; Belfer, A. J.; Locke, D. C. Measurement of limiting activity coefficients using non-steady-state gas chromatography. *Ind. Eng. Chem. Res.* **1991**, *30*, 1900–1906.
- (17) Zhou, X.; Mopper, K. Apparent partition coefficients of 15 carbonyl compounds between air and seawater and between air and freshwater; implications for air-sea exchange. *Environ. Sci. Technol.* **1990**, *24*, 1864–1869.
- (18) Lichenbelt, J. H.; Schram, B. J. Vapor-liquid equilibrium of water-acetone-air at ambient temperatures and pressures. An analysis of different VLE-fitting methods. *Ind. Eng. Chem. Process Des. Dev.* **1985**, *24*, 391–397.
- (19) Snider, J. R.; Dawson, G. A. Tropospheric light alcohols, carbonyls, and acetonitrile: concentrations in the southwestern United States and Henry's law data. *J. Geophys. Res.* **1985**, *90*, 3793–3805.
- (20) Mash, C. J.; Pemberton, R. C. Activity coefficients at very low concentrations for organic solutes in water determined by an automatic chromatographic method. *NPL Rep. Chem.* **1980**, *111*, 23.
- (21) Vitenberg, A. G.; Ioffe, B. V.; Dimitrova, Z. S.; Butaeva, I. L. Determination of gas-liquid partition coefficients by means of gas chromatographic analysis. *J. Chromatogr.* **1975**, *112*, 319–327.
- (22) Buttery, R. G.; Ling, L. C.; Guadagni, D. G. Volatilities of aldehydes, ketones, and esters in dilute water solution. *J. Agric. Food Chem.* **1969**, *17*, 385–389.
- (23) Burnett, M. G. Determination of partition coefficients at infinite dilution by the gas chromatographic analysis of the vapor above dilute solutions. *Anal. Chem.* **1963**, *35*, 1567–1570.
- (24) Burnett, M. G.; Swoboda, P. A. T. A simple method for the calibration of sensitive gas chromatographic detectors. *Anal. Chem.* **1962**, *34*, 1162–1163.
- (25) Butler, J. A. V.; Ramchandani, C. N. The solubility of nonelectrolytes. Part II. The influence of the polar group on the free energy of hydration of aliphatic compounds. *J. Chem. Soc.* **1935**, 952–955.
- (26) Ashworth, R. A.; Howe, G. B.; Mullins, M. E.; Rogers, T. N. Air-water partitioning coefficients of organics in dilute aqueous solutions. *J. Hazard. Mater.* **1988**, *18*, 25–36.
- (27) Park, J. H.; Hussam, A.; Couason, P.; Fritz, D.; Carr, P. W. Experimental reexamination of selected partition coefficients from Rohrschneider's data set. *Anal. Chem.* **1987**, *59*, 1970–1976.
- (28) Sorrentino, F.; Voilley, A.; Richon, D. Activity coefficients of aroma compounds in model food systems. *AIChE J.* **1986**, *32*, 1988–1993.
- (29) Richon, D.; Sorrentino, F.; Voilley, A. Infinite dilution activity coefficients by inert gas stripping method: extension to the study of viscous and foaming mixtures. *Ind. Eng. Chem. Process Des. Dev.* **1985**, *24*, 1160–1165.
- (30) Aarna, A. Ya.; Melder, L. I.; Ebber, A. V. Gas-chromatographic determination of thermodynamic functions of solution of ketones and ethers. *J. Appl. Chem. USSR* **1979**, *52*, 1558–1560.
- (31) Sato, A.; Nakajima, T. Partition coefficients of some aromatic hydrocarbons and ketones in water, blood and oil. *Br. J. Ind. Med.* **1979**, *36*, 231–234.
- (32) Shiu, W.-Y.; Mackay, D. Henry's law constants of selected aromatic hydrocarbons, alcohols, and ketones. *J. Chem. Eng. Data* **1997**, *42*, 27–30.
- (33) Arce, A.; Blanco, A.; Souza, P.; Vidal, I. Liquid-liquid equilibria of the ternary mixtures water + propanoic acid + methyl ethyl ketone and water + propanoic acid + methyl propyl ketone. *J. Chem. Eng. Data* **1995**, *40*, 225–229.
- (34) Stephenson, R. M. Mutual solubilities: water-ketones, water-ethers, and water-gasoline-alcohols. *J. Chem. Eng. Data* **1992**, *37*, 80–95.
- (35) Ferino, I.; Marongiu, B.; Solinas, V.; Torrazza, S. Thermodynamic properties of aqueous nonelectrolyte mixtures. II. Excess enthalpies and liquid-liquid equilibrium of 2-alkanone + water mixtures. *Thermochim. Acta* **1983**, *70*, 149–161.
- (36) Sørensen, J. M.; Arlt, W. *Liquid-Liquid Equilibrium Data Collection*; DECHEMA: Frankfurt, 1979.
- (37) Nelson, P. E.; Hoff, J. E. Food volatiles: gas chromatographic determination of partition coefficients in water-lipid systems. *J. Food Sci.* **1968**, *33*, 479–482.
- (38) Correa, J. M.; Blanco, A.; Arce, A. Liquid-liquid equilibria of the system water + acetic acid + methyl isopropyl ketone between 25 and 55 °C. *J. Chem. Eng. Data* **1989**, *34*, 415–419.
- (39) Stephenson, R. M.; Malanowski, S. *Handbook of the Thermodynamics of Organic Compounds*; Elsevier: New York, 1987.
- (40) Dewulf, J.; Langenhove, H. V.; Everaert, P. Determination of Henry's law coefficients by combination of the equilibrium partitioning in closed systems and solid-phase microextraction techniques. *J. Chromatogr. A* **1999**, *830*, 353–363.
- (41) Feki, M.; Fourati, M.; Chaabouni, M. M.; Ayedi, H. F. Purification of wet process phosphoric acid by solvent extraction liquid-liquid equilibrium at 25 and 40 °C of the system water-phosphoric acid-methylisobutyl ketone. *Can. J. Chem. Eng.* **1994**, *72*, 939–944.
- (42) Guetachew, T.; Mokbel, I.; Meile, J.-P.; Jose, J. Vapor pressures and sublimation pressures of naphthalene and of five alkan-2-ones (C4, C5, C7, C8, C9) at pressures in the range 0.3 Pa to 160 kPa. *ELDATA Int. Electron. J. Phys.-Chem. Data* **1995**, *1*, 249–254.
- (43) Tewari, Y. B.; Miller, M. M.; Wasik, S. P.; Martire, D. E. Aqueous solubility and octanol/water partition coefficient of organic compounds at 25.0 °C. *J. Chem. Eng. Data* **1982**, *27*, 451–454.
- (44) Li, J.; Carr, P. W. Measurement of water-hexadecane partition coefficients by headspace gas chromatography and calculation of limiting activity coefficients in water. *Anal. Chem.* **1993**, *65*, 1443–1450.
- (45) Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds*; Blackwell: Oxford, 1985.
- (46) Pfeiffer, Th.; Löwen, B.; Schulz, S. Calorimetric measurement of the partial molar excess enthalpy at infinite dilution  $h^{E,\infty}$  and its meaning for the calculation of the concentration and temperature dependence of the molar excess enthalpy  $h^E$ . *Fluid Phase Equilib.* **1995**, *106*, 139–167.
- (47) Dohnal, V.; Roux, A. H.; Hynek, V. Limiting partial molar excess enthalpies by flow calorimetry: some organic solvents in water. *J. Solution Chem.* **1994**, *23*, 889–900.
- (48) French, H. T. Excess enthalpies of (acetone+water) at 278.15, 288.15, 298.15, 308.15, 318.15, and 323.15 K. *J. Chem. Thermodyn.* **1989**, *21*, 801–809.
- (49) Della Gatta, G.; Stradella, L.; Venturello, P. Enthalpies of solvation in cyclohexane and in water for homologous aliphatic ketones and esters. *J. Solution Chem.* **1981**, *10*, 209–220.
- (50) Duer, W. C.; Bertrand, G. L. Thermochemical isotope effects. Chloroform/ chloroform-*d* and acetone/acetone-*d* in selected solvents. *J. Am. Chem. Soc.* **1974**, *96*, 1300–1304.
- (51) Arnett, E. M.; Burke, J. J.; Carter, J. V.; Douty, C. F. Solvent effects in organic chemistry. XV. Thermodynamics of solution for nonelectrolytes in aqueous acid and salt solutions. *J. Am. Chem. Soc.* **1972**, *94*, 7837–7852.
- (52) Arnett, E. M.; McKelvey, D. R. Enthalpies of transfer from water to dimethyl sulfoxide for some ions and molecules. *J. Am. Chem. Soc.* **1966**, *88*, 2598–2599.
- (53) Hanson, D. O.; Winkle, M. V. Relation between heats of mixing and distribution of ketone between phases in some ketone-water-solvent ternaries. *J. Chem. Eng. Data* **1960**, *5*, 30–34.
- (54) Bury, R.; Lucas, M.; Barberi, P. Study of thermodynamic quantities of the transfer of a series of ketones in the gaseous state to the diluted state in water at 25 °C. *J. Chim. Phys. Phys.-Chim. Biol.* **1978**, *75*, 575–577 (in French).
- (55) Tasker, I. R.; Suri, S. K.; Wood, R. H. Heat capacities of some binary and ternary aqueous nonelectrolyte systems. *J. Chem. Eng. Data* **1984**, *29*, 193–199.
- (56) Desnoyers, J. E.; de Visser, C.; Perron, G.; Picker, P. Reexamination of the heat capacities obtained by flow microcalorimetry. Recommendation for the use of a chemical standard. *J. Solution Chem.* **1976**, *55*, 605–616.
- (57) Hovorka, S.; Roux, A. H.; Roux-Desgranges, G.; Dohnal, V. Limiting partial molar excess heat capacities and volumes of selected organic compounds in water at 25 °C. *J. Solution Chem.* **1999**, *28*, 1289–1305.
- (58) Roux, G.; Perron, G.; Desnoyers, J. E. The heat capacities and volumes of some low molecular weight amides, ketones, esters, and ethers in water over the whole solubility range. *Can. J. Chem.* **1978**, *56*, 2808–2814.
- (59) Tasker, I. R.; Spitzer, J. J.; Suri, S. K.; Wood, R. H. Volumetric properties of some aqueous nonelectrolyte solutions. *J. Chem. Eng. Data* **1983**, *28*, 266–275.
- (60) Edward, J. T.; Farrell, P. G.; Shahidi, F. Partial molar volumes of organic compounds in water. Part 1. Ethers, ketones, esters and alcohols. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 705–714.
- (61) Kiyohara, O.; Perron, G.; Desnoyers, J. Volumes and heat capacities of dimethylsulfoxide, acetone, and acetamide in water and of some electrolytes in these mixed aqueous solvents. *Can. J. Chem.* **1975**, *53*, 3263–3268.
- (62) Boje, L.; Hvidt, A. Densities of aqueous mixtures of nonelectrolytes. *J. Chem. Thermodyn.* **1971**, *3*, 663–673.
- (63) Davies, J. V.; Fooks, R.; Koga, Y. Excess partial molar volumes and thermal expansivities in the water-rich region of aqueous 2-butanone. *J. Solution Chem.* **1994**, *23*, 339–350.

Received for review August 1, 2000. Accepted November 23, 2000. This work was supported by Department of Energy (DOE) Grant DE-FG02-92ER-14297.

JE0002282