

Comparison of enthalpy, entropy, and volume changes of chemical reactions

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The enthalpy, entropy, and volume changes were compared for 63 reactions. The changes in entropy and volume are proportional to a significant extent, whereas no proportionality between the changes in enthalpy and volume of the reactions are observed.

Key words: reaction volume, reaction enthalpy, reaction entropy.

Constants of rate and equilibrium of chemical reactions increase considerably at elevated hydrostatic pressure if the activation and reaction volumes are negative.^{1–6} The activation volume is equal to the difference of volumes of the activated complex and reactants, whereas the reaction volume is equal to the difference of volumes of the products and reactants. The free activation energy and reaction energy dependences of the pressure make it possible to calculate these volume changes

$$\Delta V = \partial \Delta G / \partial P = -RT \partial \ln K / \partial P. \quad (1)$$

The free energy (ΔG) is related to the enthalpy (ΔH) and entropy (ΔS) of the reaction by the following equation

$$\Delta G = \Delta H - T\Delta S. \quad (2)$$

The enthalpy, entropy, and volume changes for the dissociation processes of 70 acids and bases in water were compared.⁷ A distinct proportionality in changing volume ($\Delta V/\text{cm}^3 \text{mol}^{-1}$) and entropy ($\Delta S/\text{J mol}^{-1} \text{K}^{-1}$) of the dissociation reactions was observed

$$\Delta S = -29.2 + 4.4\Delta V, \quad (3)$$

whereas no similar proportionality was observed for the enthalpy.⁷

This dependence (3) can be explained^{5,7} by a significant electrostriction of water molecules during solvation of the formed ions.

It was shown^{8–10} that the change in the partial molar volume (PMV) of organic molecules and salts in the series of solvent usually did not correlate with the difference in their enthalpies of dissolution. For example, the dissolution of lithium and magnesium perchlorates in polar solvents is always accompanied by a significant exothermal

effect; however, no proportionality in changing PMV and enthalpies of dissolution is observed^{8–10} (Table 1).

The volume of a dilute solution (V) can be presented as follows:

$$V = V_A N_A + V_S N_S + (V_S^* - V_S) z N_A, \quad (4)$$

where V_A , V_S , and V_S^* are the molar volumes of the solute, pure solvent, and solvent in the solvate shell, respectively; z is the number of solvent molecules in the solvate shell of the solute (A); N_A and N_S are the numbers of moles of the solute and free solvent in solution. It follows from Eq. (4)

Table 1. Enthalpies ($\Delta H_{\text{sol}}/\text{kJ mol}^{-1}$) of dissolution of anhydrous magnesium and lithium perchlorates in a series of solvents and their partial molar volumes ($V/\text{cm}^3 \text{mol}^{-1}$) at 25 °C

Solvent	$\text{Mg}(\text{ClO}_4)_2$		LiClO_4	
	$-\Delta H_{\text{sol}}$	V	$-\Delta H_{\text{sol}}$	V
Water	153	67.3	26.3	44.2
Ethyl acetate	142	46.6	37.2	25.1
Acetone	191	-2.4	—	-2.0
Formamide	190	82.3	45.2	48.3
Dimethyl sulfoxide	238	62.3	75.3	38.7
Dimethylformamide	245	42.3	—	—
Propylene carbonate	189	56.7	—	—
Nitromethane	270	63.9	61.9	36.4
Acetonitrile	198	20.3	38.5	20.1
Diethyl ether	—	24.3	25.9	14.5
Methanol	205	-4.7	51.9	24.6
Ethanol	171	2.5	—	—
Propan-1-ol	178	36.3	—	—

Note. For crystalline $\text{Mg}(\text{ClO}_4)_2$ and LiClO_4 the molar volumes are 85.8 and 43.8 $\text{cm}^3 \text{mol}^{-1}$, respectively.

that the observed value of PMV of the compound (V_{obs}) in a dilute solution is determined by the equation

$$V_{\text{obs}} = \partial V / \partial N_A = V_A + z(V_S^* - V_S). \quad (5)$$

Thus, the observed value (V_{obs}) of the molar volume of the substance (A) in solution includes the intrinsic volume V_A and the change in the solvent volume, $z(V_S^* - V_S)$, when transfers from the bulk to the solvation shell of the solute. The data in Table 1 show that the compression volume of the solvent, $z(V_S^* - V_S)$, can exceed the intrinsic volume of the salt, which results in negative values of the observed PMV. Even in the case of high heat effects of dissolution

of electrolytes, the values of their PMV in solution are significantly proportional to compressibility of the solvent ($V^{-1} \partial V / \partial P$) and its electrostriction ($\epsilon^{-2} \partial \epsilon / \partial P$) and are not proportional to changes in the enthalpy of dissolution.^{8–10}

Table 2 contains the data on the molar volume, enthalpy, and entropy of formation of a series of isomeric compounds in the liquid phase at 25 °C. Totally, 56 pairs of isomers and 7 decomposition processes were considered: $C_{(n+q)}H_{(m+r)}Y_{(p+s)} \rightarrow C_nH_mY_p + C_qH_rY_s$. These data makes it possible to compare the changes in volumes, enthalpies, and entropies of nonpolar and lowly polar reactions in the liquid phase in the absence of solvent.

Table 2. Molar volumes ($V/\text{cm}^3 \text{mol}^{-1}$), enthalpy ($\Delta H_{\text{form}}/\text{kJ mol}^{-1}$), and entropy ($\Delta S_{\text{form}}/\text{J mol}^{-1} \text{K}^{-1}$) of formation of the reactants (R) and reaction products (P) and changes in the volumes ($\Delta V_{r-n}/\text{cm}^3 \text{mol}^{-1}$), enthalpy ($\Delta H_{r-n}/\text{kJ mol}^{-1}$), and entropy ($\Delta S_{r-n}/\text{J mol}^{-1} \text{K}^{-1}$) of these processes in the liquid phase

Reaction	$\Delta V_{r-n} = \Sigma V_P - \Sigma V_R$	$\Delta H_{r-n} = \Sigma \Delta H_{\text{form,P}} - \Sigma \Delta H_{\text{form,R}}$	$\Delta S_{r-n} = \Sigma \Delta S_{\text{form,P}} - \Sigma \Delta S_{\text{form,R}}$
Acetonitrile → methyl isocyanide	2.78 = 55.03 – 52.25	64.45 = 117.6 – 53.15	—
1,2-Dichloroethane → 1,1-dichloroethane	4.1 = 84.23 – 80.13	4.2 = –160.8 – (–165)	3.2 = 211.8 – 208.6
Acetic acid → methyl formate	4.41 = 61.65 – 57.24	105.9 = –378.3 – (–484.2)	—
Methyl sulfide → ethanethiol	0.61 = 74.05 – 73.44	–8.3 = –73.7 – (–65.4)	10.7 = 207.1 – 196.4
Ethanedithiol → methyl disulfide	5.09 = 88.87 – 83.78	–8.9 = –62.6 – (–53.7)	—
1,2-Dimethylhydrazine → → 1,1-dichloroethane	3.33 = 75.97 – 72.64	–0.8 = 49.8 – 50.6	1.1 = 200.3 – 199.2
Ethylenediamine → 1,2-dimethylhydrazine	5.91 = 72.64 – 66.73	77.2 = 50.6 – (–26.6)	—
Ethylenediamine → 1,1-dimethylhydrazine	9.24 = 75.97 – 66.73	76.4 = 49.8 – (–26.6)	—
Prop-2-yn-1-ol → acrolein	7.6 = 66.71 – 59.11	–100.3 = –122.1 – (–21.8)	—
Propylene oxide → acetone	3.45 = 73.33 – 69.88	–127.5 = –248.2 – (–120.7)	4.2 = 200.5 – 196.3
Propyl alcohol → isopropyl alcohol	1.8 = 76.51 – 74.71	–13.5 = –318.1 – (–304.6)	–12.3 = 180.6 – 192.9
Propanethiol → ethyl methyl sulfide	0.01 = 90.56 – 90.55	8.3 = –91.6 – (–99.9)	–3.5 = 239.1 – 242.6
Propanethiol → propane-2-thiol	2.98 = 93.53 – 90.55	–6.0 = –105.9 – (–99.9)	–9.0 = 233.6 – 242.6
Ethyl methyl sulfide → propane-2-thiol	2.97 = 93.53 – 90.56	–14.3 = –105.9 – (–91.6)	–5.5 = 233.6 – 239.1
Buta-1,2-diene → buta-1,3-diene	4.12 = 87.08 – 82.96	–53.5 = 85.4 – 138.9	–10.6 = 199.1 – 209.7
Buta-1,2-diene → but-2-yne	0.12 = 83.08 – 82.96	–19.0 = 119.9 – 138.9	–14.6 = 195.1 – 209.7
But-2-yne → buta-1,3-diene	4 = 87.08 – 83.08	–34.5 = 85.4 – 119.9	4.0 = 199.1 – 195.1
Butan-2-one → butyraldehyde	0.15 = 89.68 – 89.53	34.5 = –238.8 – (–273.3)	8.0 = 246.9 – 238.9
1,4-Dioxane → butanoic acid	6.77 = 91.99 – 85.22	–180.4 = –534.0 – (–353.6)	31.1 = 226.4 – 195.3
1,4-Dioxane → ethyl acetate	12.6 = 97.82 – 85.22	–125.5 = –479.1 – (–353.6)	64.2 = 259.5 – 195.3
Butanoic acid → ethyl acetate	5.83 = 97.82 – 91.99	54.9 = –479.1 – (–534.0)	33.1 = 259.5 – 226.4
Butan-1-ol → <i>tert</i> -butanol	2.43 = 93.98 – 91.55	–33.5 = –359.4 – (–325.9)	–32.6 = 193.2 – 225.8
<i>tert</i> -Butanol → ethyl ether	9.83 = 103.81 – 93.98	79.8 = –279.6 – (–359.4)	60.0 = 253.2 – 193.2
Butan-1-ol → ethyl ether	12.26 = 103.81 – 91.55	46.3 = –279.6 – (–325.9)	27.4 = 253.2 – 225.8
Butane-1-thiol → ethyl sulfide	0.2 = 107.36 – 107.16	5.3 = –119.4 – (–124.7)	–6.7 = 269.3 – 276.0
Butane-1-thiol → methylisopropyl sulfide	1.5 = 108.66 – 107.16	0 = –124.7 – (–124.7)	–12.8 = 263.2 – 276.0
Butane-1-thiol → methylpropyl sulfide	0.2 = 107.36 – 107.16	6.6 = –118.1 – (–124.7)	–3.4 = 272.6 – 276.0
Ethyl sulfide → methylisopropyl sulfide	1.3 = 108.66 – 107.36	–5.4 = –124.7 – (–119.3)	–6.1 = 263.2 – 269.3
Ethyl sulfide → methylpropyl sulfide	0 = 107.36 – 107.36	1.3 = –118.1 – (–119.4)	3.3 = 272.6 – 269.3
Methyl propyl sulfide → → methylisopropyl sulfide	1.3 = 108.66 – 107.36	–6.6 = –124.7 – (–118.1)	–9.4 = 263.2 – 272.6
Cyclopentene → isoprene	11.86 = 100.09 – 88.23	45.1 = 49.4 – 4.3	28.1 = 229.4 – 201.3
Cyclopentene → penta-1,4-diene	14.85 = 103.08 – 88.23	71.3 = 75.6 – 4.3	42.3 = 243.6 – 201.3
Cyclopentene → spiropentane	1.98 = 90.21 – 88.23	153.3 = 157.6 – 4.3	–7.6 = 193.7 – 201.3
Isoprene → penta-1,4-diene	2.99 = 103.08 – 100.09	26.2 = 75.6 – 49.4	14.2 = 243.6 – 229.4
Spiropentane → isoprene	9.88 = 100.09 – 90.21	–108.2 = 49.4 – 157.6	35.7 = 229.4 – 193.7
Spiropentane → penta-1,4-diene	12.87 = 103.08 – 90.21	–82.0 = 75.6 – 157.6	49.9 = 243.6 – 193.7
Циклопентан → 2-метилбут-1-ен	13.75 = 107.83 – 94.08	43.4 = –62.5 – (–105.9)	49.7 = 254.0 – 204.3

(to be continued)

Table 2 (continued)

Reaction	$\Delta V_{r-n} = \Sigma V_P - \Sigma V_R$	$\Delta H_{r-n} = \Sigma \Delta H_{\text{form},P} - \Sigma \Delta H_{\text{form},R}$	$\Delta S_{r-n} = \Sigma \Delta S_{\text{form},P} - \Sigma \Delta S_{\text{form},R}$
2-Methylbut-1-ene → pent-1-ene	1.66 = 109.49 – 107.83	15.8 = –46.7 – (–62.5)	8.6 = 262.6 – 254.0
Cyclopentane → pent-1-ene	15.41 = 109.49 – 94.08	59.2 = –46.7 – (–105.9)	58.3 = 262.6 – 204.3
Pentanethiol → ethylpropyl sulfide	1.02 = 123.62 – 122.6	4.9 = –144.7 – (–149.6)	–0.8 = 309.6 – 310.4
Aniline → 2-picoline	7.48 = 98.62 – 91.14	25.4 = 56.5 – 31.1	26.6 = 217.9 – 191.3
Cyclohexane → 2,3-dimethylbut-2-ene	10.63 = 118.72 – 108.09	53.9 = –102.4 – (–156.3)	65.9 = 270.3 – 204.4
2,3-Dimethylbut-2-ene → hex-1-ene	6.31 = 125.03 – 118.72	30.0 = –72.4 – (–102.4)	25.0 = 295.3 – 270.3
Cyclohexane → hex-1-ene	16.94 = 125.03 – 108.09	83.9 = –72.4 – (–156.3)	90.9 = 295.3 – 204.4
2,3-Dimethylbut-2-ene → 2-methylpent-1-ene	5.06 = 123.78 – 118.72	12.4 = –90.0 – (–102.4)	–
2-Methylpent-1-ene → hex-1-ene	1.25 = 125.03 – 123.78	17.6 = –72.4 – (–90.0)	–
Cyclohexane → 2-methylpent-1-ene	15.69 = 123.78 – 108.09	66.3 = –90.0 – (–156.3)	–
Hexan-1-ol → isopropyl ether	14.74 = 140.32 – 125.58	28.2 = –351.3 – (–379.5)	7.5 = 294.6 – 287.1
Cycloheptane → hept-1-ene	19.62 = 140.86 – 121.24	60.1 = –98.0 – (–158.1)	85.1 = 327.7 – 242.6
Methylcyclohexane → hept-1-ene	13.24 = 140.86 – 127.62	92.2 = –98.0 – (–190.2)	79.7 = 327.7 – 248.0
Cycloheptane → methylcyclohexane	6.38 = 127.62 – 121.24	–32.1 = –190.2 – (–158.1)	5.4 = 248.0 – 242.6
Cyclooctatetraene → styrene	1.82 = 114.95 – 113.13	–151.1 = 103.9 – (–255.0)	17.3 = 237.6 – 220.3
Cyclooctane → oct-1-ene	22.57 = 156.96 – 134.39	45.7 = –123.5 – (–169.2)	98.4 = 360.5 – 262.1
Cyclodecane → dec-1-ene	28.31 = 189.34 – 161.03	32.8 = –174.6 – (–207.4)	–
Cyclodecane → butylcyclohexane	14.47 = 175.5 – 161.03	–55.9 = –263.3 – (–207.4)	–
Butylcyclohexane → dec-1-ene	13.84 = 189.34 – 175.5	88.7 = –174.6 – (–263.3)	80.0 = 425.1 – 345.1
<i>n</i> -Dodecane → <i>n</i> -hexane + hex-1-ene	28.0 = 131.7 + 125.5 – – 229.2	80.3 = –198.9 – 72.4 – – (–351.6)	100.7 = 296.1 + 295.3 – – 490.7
Octan-2-ol → water + oct-1-ene	16 = 18 + 156.9 – – 158.9	15.9 = –285.8 – – 123.5 – (–425.2)	–
<i>n</i> -Tetradecane → hex-1-ene + <i>n</i> -octane	27.6 = 125.5 + 162.4 – – 260.3	81.2 = –72.4 – 249.8 – – (–403.4)	100.7 = 360.9 + + 295.3 – 555.5
<i>n</i> -Tetradecane → <i>n</i> -hexane + oct-1-ene	28.3 = 131.7 + + 156.9 – 260.3	81.1 = –198.8 – 123.5 – – (–403.4)	101.1 = 296.1 + + 360.5 – 555.5
<i>n</i> -Hexadecane → hex-1-ene + <i>n</i> -decane	27.7 = 125.5 + 194.9 – – 292.7	83.3 = –72.4 – 300.9 – – (–456.6)	101.5 = 295.3 + + 426 – 619.8
<i>n</i> -Heptadecane → → hex-1-ene + <i>n</i> -undecane	27.8 = 125.5 + + 211.2 – 308.9	80.8 = –72.4 – – 326.8 – (–480)	101.4 = 295.3 + + 458.2 – 652.1
<i>n</i> -Hexadecane → → oct-1-ene + <i>n</i> -octane	26.6 = 156.9 + + 162.4 – 292.7	82.9 = –123.5 – – 249.8 – (–456.2)	101.6 = 360.5 + + 360.9 – 619.8

In all cases (see Table 2), the reactants and reaction products were written in such an order that the reaction volumes would be positive. The data on the molar volumes (V),¹¹ enthalpies (ΔH_{form}),^{12,13} and entropies (ΔS_{form})¹² of formation for each compound in the liquid phase make it possible to calculate the changes in the volume (ΔV_{r-n}), enthalpy (ΔH_{r-n}), and entropy (ΔS_{r-n}) for these reactions.

The changes in the volumes and enthalpies are presented in Fig. 1. Figure 2 shows the changes in the volumes and entropies of the considered reactions.

The data obtained allow us to conclude that for lowly polar reactions in the absence of solvent high changes in the enthalpy of the reaction (333 kJ mol^{–1}, from –180 kJ mol^{–1} for the reaction 1,4-dioxane → butanoic acid to +153 kJ mol^{–1} for the reaction cyclopentene → spiropentane, see Table 2) do not determine changes in the volumes of these reactions ($R = 0.38$, see Fig. 1).

The maximum change in the entropy (134.2 J mol^{–1} K^{–1}, from –32.6 J mol^{–1} K^{–1} for the reaction butan-1-ol → *tert*-butanol to +101.6 J mol^{–1} K^{–1} for the reaction

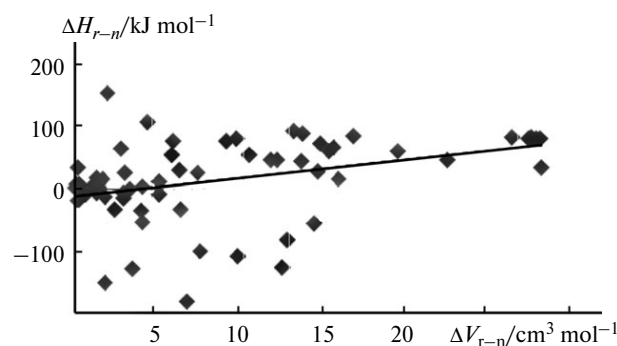


Fig. 1. Comparison of the enthalpy ($\Delta H_{r-n}/\text{kJ mol}^{-1}$) and volume ($\Delta V_{r-n}/\text{cm}^3 \text{mol}^{-1}$) changes for the reactions presented in Table 2 ($y = 3x - 12$, $R = 0.38$, $N = 63$).

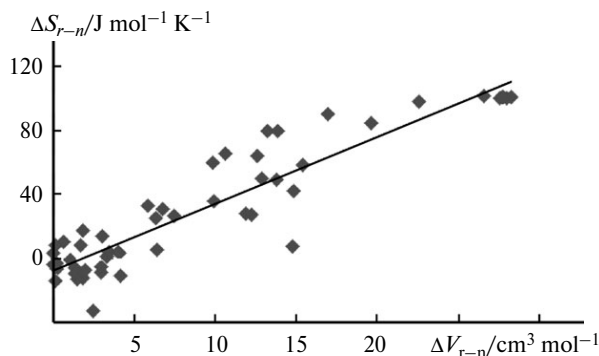


Fig. 2. Comparison of the entropy ($\Delta S_{r-n}/\text{J mol}^{-1} \text{K}^{-1}$) and volume ($\Delta V_{r-n}/\text{cm}^3 \text{mol}^{-1}$) changes for the reactions presented in Table 2 ($y = 4.2x - 7$, $R = 0.92$, $N = 51$).

n-hexadecane \rightarrow oct-1-ene + *n*-octane, see Table 2) corresponds to the energy contribution $T\Delta S_{r-n}$ equal to 40 kJ mol⁻¹ only. This entropy contribution is significantly proportional to the change in the volume of the non-polar and lowly polar reactions ($R = 0.92$, see Fig. 2). It should be mentioned that the angular coefficient of the plot of ΔS_{r-n} vs ΔV_{r-n} for molecular transformations equal to 4.2 (see Fig. 2) almost coincides with the data obtained for the dissociation acids and bases in water (4.4 in Eq. (3)). The obtained correlations have no reliable explanations at present.⁷

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