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# Inorganic Reactions of Iodine(III) in Acidic Solutions and Free Energy of Iodous Acid Formation

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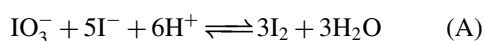
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**ABSTRACT:** An analysis of the former works devoted to the reactions of I(III) in acidic non-buffered solutions gives new thermodynamic and kinetic information. At low iodide concentrations, the rate law of the reaction  $\text{IO}_3^- + \text{I}^- + 2\text{H}^+ \rightleftharpoons \text{IO}_2\text{H} + \text{IOH}$  is  $k_{+B} [\text{IO}_3^-][\text{I}^-][\text{H}^+]^2 - k_{-B} [\text{IO}_2\text{H}][\text{IOH}]$  with  $k_{+B} = 4.5 \times 10^3 \text{ M}^{-3}\text{s}^{-1}$  and  $k_{-B} = 240 \text{ M}^{-1}\text{s}^{-1}$  at 25°C and zero ionic strength. The rate law of the reaction  $\text{IO}_2\text{H} + \text{I}^- + \text{H}^+ \rightleftharpoons 2\text{IOH}$  is  $k_{+C} [\text{IO}_2\text{H}][\text{I}^-][\text{H}^+] - k_{-C} [\text{IOH}]^2$  with  $k_{+C} = 1.9 \times 10^{10} \text{ M}^{-2}\text{s}^{-1}$  and  $k_{-C} = 25 \text{ M}^{-1}\text{s}^{-1}$ . These values lead to a Gibbs free energy of  $\text{IO}_2\text{H}$  formation of  $-95 \text{ kJ mol}^{-1}$ . The  $\text{pK}_a$  of iodous acid should be about 6, leading to a Gibbs free energy of  $\text{IO}_2^-$  formation of about  $-61 \text{ kJ mol}^{-1}$ . Estimations of the four rate constants at 50°C give, respectively,  $1.2 \times 10^4 \text{ M}^{-3}\text{s}^{-1}$ ,  $590 \text{ M}^{-1}\text{s}^{-1}$ ,  $2 \times 10^9 \text{ M}^{-2}\text{s}^{-1}$ , and  $20 \text{ M}^{-1}\text{s}^{-1}$ . Mechanisms of these reactions involving the protonation  $\text{IO}_2\text{H} + \text{H}^+ \rightleftharpoons \text{IO}_2\text{H}_2^+$  and an explanation of the decrease of the last two rate constants when the temperature increases, are proposed. © 2008 Wiley Periodicals, Inc. *Int J Chem Kinet* 40: 647–652, 2008

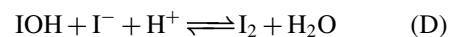
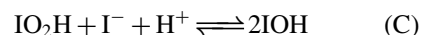
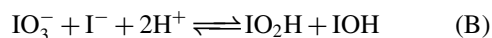
## INTRODUCTION

Reaction (A) is of environmental interest in the evaluation of the consequences of a nuclear reactor accident [1–4] and in oceanic studies [5–8] and is part of several chemical oscillators, the Bray–Liebhafsky reaction [9–15], the Briggs–Rauscher reaction [9,16–22], and oscillators derived from the chlorite–iodide reaction [23–26] and from iodate reactions with reducing agents [27–32].



Its mechanism depends on the experimental conditions and is not completely elucidated despite a large num-

ber of kinetic studies [33–36]. This paper presents an analysis of the information available under the conditions of the oscillatory Bray–Liebhafsky reaction, i.e., in acidic nonbuffered solutions with an iodide concentration lower than  $10^{-7} \text{ mol L}^{-1}$ . Reaction (A) is the combination of three reactions, (B) + (C) + 3 × (D), but they are themselves complicated.



We have discussed the kinetics and mechanism of reactions (–C) and (D) in a former work [37] and discuss here reactions (B) and (+C).

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# KINETICS AND THERMODYNAMICS OF REACTIONS (B) AND (C) AT 25°C

Under the experimental conditions considered in this paper, the rate law of reaction (+B) is [36]

$$r_{+B} = k_{+B} [\text{IO}_3^-][\text{I}^-][\text{H}^+]^2 \quad (1)$$

A mechanism of reaction (B) is proposed in the appendix but has no effect on the following analysis. The essential is the criterion of internal consistency of reaction mechanisms [38]. When a reaction is at equilibrium, thermodynamics gives an expression relating concentrations (activities) to its equilibrium constant  $K$  and kinetics gives another expression, the equality of the rates in the forward and backward directions. These two expressions must be strictly equivalent even if the reaction is not elementary. Thus, under conditions such that the rate law of reaction (+B) is (1), the rate law of reaction (−B) must be (2), with  $k_{+B}/k_{-B} = K_B$ .

$$r_{-B} = k_{-B} [\text{IO}_2\text{H}][\text{IOH}] \quad (2)$$

The rate law (3) is also well established [37].

$$r_{-C} = k_{-C} [\text{IOH}]^2 \quad (3)$$

Then, the rate law of reaction (C) in the forward direction must be (4) with  $k_{+C}/k_{-C} = K_C$ .

$$r_{+C} = k_{+C} [\text{IO}_2\text{H}][\text{I}^-][\text{H}^+] \quad (4)$$

A mechanism of reaction (C) is also proposed in the appendix. The product\*  $K_B^\circ K_C^\circ$ , equal to  $k_{+B}^\circ k_{+C}^\circ / k_{-B}^\circ k_{-C}^\circ$ , is obtained from the accurately known thermodynamic equilibrium constants of reactions (A) and (D):  $K_A^\circ = (9.8 \pm 0.2) \times 10^{46}$  [39,40] and  $1/K_D^\circ = (5.3 \pm 0.1) \times 10^{-13}$  at 25°C [37].

$$K_B^\circ K_C^\circ = K_A^\circ / (K_D^\circ)^3 = (1.5 \pm 0.5) \times 10^{10} \quad (5)$$

At 25°C and 0.2 M ionic strength,  $k_{+B} = 1250 \text{ M}^{-3}\text{s}^{-1}$  [36]. The activity coefficient  $\gamma$  is about 0.70–0.75 at this ionic strength,<sup>†</sup> giving  $k_{+B}^\circ = k_{+B}/\gamma^4 = (4\text{--}5) \times 10^3 \text{ M}^{-3}\text{s}^{-1}$  in agreement with the value  $4.7 \times 10^3 \text{ M}^{-3}\text{s}^{-1}$  obtained by Furuichi and Liebafsky [42]. The value  $k_{-C}^\circ = 25 \text{ M}^{-1}\text{s}^{-1}$  is also well known [37,43]. With the value  $k_{-B}^\circ = 240 \text{ M}^{-1}\text{s}^{-1}$  obtained by Furrow

**Table I** Used and Estimated Thermodynamic Values

	$\Delta H_f^\circ$ (kJ mol <sup>−1</sup> )	$S^\circ$ (J mol <sup>−1</sup> K <sup>−1</sup> )	$\Delta G_f^\circ$ (kJ mol <sup>−1</sup> )
I <sub>2</sub> (aq.) <sup>a</sup>	20.92	131.2	16.43
I <sup>−a</sup>	−56.78	106.45	−51.72
IOH <sup>b</sup>	−138.1	95.4	−99.2
IOH <sup>c</sup>	−138.1	94.7	−98.9
IO <sub>2</sub> H <sup>d</sup>		140 ± 20	−95
IO <sub>2</sub> <sup>−d</sup>			−61

<sup>a</sup> From [45,46].

<sup>b</sup> From [47].

<sup>c</sup> From  $K_D$  and  $d \ln(K_D)/d(1/T)$  at 25° [37].

<sup>d</sup> This work.

[43] and Noszticzius et al. [44], Eq. (5) allows the calculation

$$k_{+C}^\circ = 1.9 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$$

This rate constant has not been measured directly, but Furrow [43] has proposed  $r_{+C} = 5 \times 10^9 [\text{IO}_2\text{H}][\text{I}^-]$  in 0.30 M H<sub>2</sub>SO<sub>4</sub>, which gives about our value of  $k_{+C}$  for the correct rate law, and similar values were adopted in numerical simulations of different systems [27,29,30]. The mechanism discussed in the appendix explains this very large value of  $k_{+C}^\circ$ .

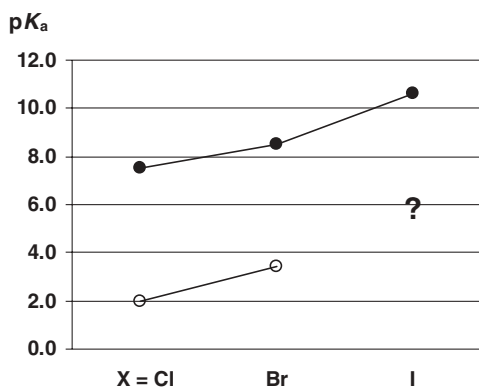
The above rate constants allow an estimation of the free energy of IO<sub>2</sub>H formation. The thermodynamic relation between the equilibrium constant  $K_C^\circ$  and the free energies of reactants and products formation,  $RT \ln(K_C^\circ) = -2 \times \Delta G_f^\circ(\text{IOH}) + \Delta G_f^\circ(\text{I}^-) + \Delta G_f^\circ(\text{IO}_2\text{H})$ , with  $K_C^\circ = k_{+C}^\circ/k_{-C}^\circ = 7.5 \times 10^8$  and  $\Delta G_f^\circ$  values in Table I gives

$$\Delta G_f^\circ(\text{IO}_2\text{H}) = -95 \text{ kJ mol}^{-1}$$

Stanisavljev [48] has proposed a correlation between thermodynamic values of oxo-halogen ions and has obtained  $\Delta G_f^\circ(\text{IO}_2^-) = -51.8 \text{ kJ mol}^{-1}$ . He has also estimated the dissociation constant of IO<sub>2</sub>H,  $pK_a(\text{IO}_2\text{H}) = 4$ , and obtained  $\Delta G_f^\circ(\text{IO}_2\text{H}) = -75 \text{ kJ mol}^{-1}$ . However, this value introduced in the above equation leads to  $K_C^\circ = 2.8 \times 10^{12}$  and an impossibly large value of  $k_{+C}^\circ$ . His correlation supports the idea that  $k_{+C}^\circ$  is very large but overestimates  $\Delta G_f^\circ(\text{IO}_2^-)$  and probably also the dissociation constant of IO<sub>2</sub>H. Figure 1 shows known  $pK_a$  values of oxy-halogen acids, including the value of  $pK_a(\text{BrO}_2\text{H})$  [49] not considered by Stanisavljev, and suggests that  $pK_a(\text{IO}_2\text{H})$  is closer to 6 than to 4. Our value of  $\Delta G_f^\circ(\text{IO}_2\text{H})$  with  $pK_a(\text{IO}_2\text{H}) = 6$  gives  $\Delta G_f^\circ(\text{IO}_2^-) = -61 \text{ kJ mol}^{-1}$ .

\*Superscripts ° denote thermodynamic constants or kinetic constants extrapolated at zero ionic strength.

<sup>†</sup>The activity coefficients can be estimated using Pitzer's correlation [41]. We neglected the effect of ionic strength on isocoulombic reactions.



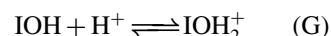
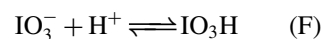
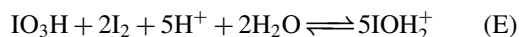
**Figure 1**  $pK_a$  values of oxy-halogen compounds  $XOH$  (●) and  $XO_2H$  (○).

### EVALUATION OF THE RATE CONSTANTS AT 50°C

The Bray–Liebhafsky oscillating reaction is very slow at 25°C and is usually studied at 50°C. Although the information about the rate constants of reactions (B) and (C) at 50° is partial, an estimation is possible.  $1/K_D^\circ = 4.7 \times 10^{-12}$  [37] and  $K_A^\circ = 2 \times 10^{43}$  [39, 40] gives  $K_A^\circ/(K_D^\circ)^3 = k_{+B}^\circ k_{+C}^\circ / k_{-B}^\circ k_{-C}^\circ = 2.1 \times 10^9$  at 50°C. The value of  $k_{-C}^\circ$  decreases slowly when the temperature increases [37] and is about  $20 \text{ M}^{-1} \text{ s}^{-1}$  at 50°C. The activation energy reported by Furuichi and Liebhafsky [42],  $E/R = 3\,720 \text{ K}$ , gives  $k_{+B}^\circ = 1.2 \times 10^4 \text{ M}^{-3} \text{ s}^{-1}$ . The effect of the temperature on the values of  $k_{+C}^\circ$  and  $k_{-B}^\circ$  is unknown, but orders of magnitude can be deduced from the standard entropy of  $IO_2H$  as follows. Starting from the standard entropy of  $IOH$  equal to  $95 \text{ J mol}^{-1} \text{ K}^{-1}$ , we note that the addition of one oxygen atom to similar compounds results in an increase of  $30\text{--}60 \text{ J mol}^{-1} \text{ K}^{-1}$ . Thus, we estimate the standard entropy of  $IO_2H$  as  $140 \pm 20 \text{ J mol}^{-1} \text{ K}^{-1}$ . This value and other values in Table I allow calculating the entropy of reaction (C) at 25°C,  $\Delta S_{r,C}^\circ = -57 \text{ J mol}^{-1} \text{ K}^{-1}$ , then its enthalpy  $\Delta H_{r,C}^\circ = T \Delta S_{r,C}^\circ - RT \ln(K_C^\circ) = -68 \text{ kJ mol}^{-1}$ . Neglecting the differences between the heat capacities, these values give  $K_C^\circ = 1.0 \times 10^8$  at 50°C. The same calculations using  $S^\circ(IO_2H) = 120 \text{ J mol}^{-1} \text{ K}^{-1}$  give  $\Delta S_{r,C}^\circ = -37 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $\Delta H_{r,C}^\circ = -62 \text{ kJ mol}^{-1}$ , and  $K_C^\circ = 1.2 \times 10^8$  at 50°C. Thus, an error of  $20 \text{ J mol}^{-1} \text{ K}^{-1}$  on the value of the standard entropy of  $IO_2H$  results in an error of 20% on  $K_C$ . As the uncertainties affecting the parameters values used when modeling systems mentioned in the introduction are often much larger than 20%, this result is meaningful. It gives  $K_B^\circ = 20$ ,  $k_{+C}^\circ = K_C^\circ \times k_{-C}^\circ = 2.1 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$  and  $k_{-B}^\circ = k_{+B}^\circ / K_B^\circ = 590 \text{ M}^{-1} \text{ s}^{-1}$ . We explain in the appendix the decrease of  $k_{+C}^\circ$  when the temperature increases.

### IODINE(I) AND IODINE(III) IN CONCENTRATED SULFURIC ACID SOLUTIONS

Thermodynamic estimations throw some light on the formation of I(I) and I(III) from iodate and iodine in concentrated sulfuric acid solutions studied experimentally by Noszticzius et al. [44]. Reaction (E) is the combination (A) –  $5 \times$  (D) – (F) +  $5 \times$  (G).



The above values of  $K_A$  and  $K_D$  with  $1/K_F = 0.156 \text{ M}$  [50,51] and  $K_G = 0.5 \text{ M}^{-1}$  [37] give

$$K_E^\circ = \frac{a_{IOH_2^+}^5}{a_{IO_3H} a_{I_2}^2 a_{H^+}^5 a_w^2} = 2 \times 10^{-17} \text{ M}^{-3}$$

The activity of the proton  $a_{H^+}$  is given by the Hammett acidity function [52,53]

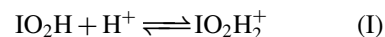
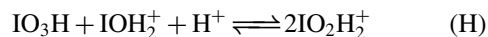
$$H_0 = -\log a_{H^+} \gamma_B / \gamma_{BH^+}$$

where  $\gamma_B / \gamma_{BH^+}$  is the ratio of the activity coefficients of the nonprotonated and protonated forms of an indicator with the assumption that this ratio is the same for all indicators of the same charge type. We assume that it is also the ratio  $\gamma_{IOH} / \gamma_{IOH_2^+}$ . In 96% sulfuric acid,  $H_0 = -10$  [53], and the activity of water  $a_w$  is  $1.4 \times 10^{-5}$  [54]. The equilibrium concentration of I(I) in a mixture of iodate and iodine is given by

$$\frac{[IOH_2^+]^5}{[IO_3H][I_2]^2} = K_E^\circ a_w^2 \times 10^{-5H_0} \frac{\gamma_{IO_3H} \gamma_{I_2}^2}{\gamma_{IOH}^5}$$

where  $K_E^\circ a_w^2 \times 10^{-5H_0} = 4 \times 10^{23}$ . The very high value of  $a_{H^+}$  in concentrated sulfuric acid solutions shifts reaction (E) completely to the right.

Reaction (H) is the combination (B) – (C) – (F) – (G) +  $2 \times$  (I).



Furrow has observed that the rate of  $IO_2H$  disproportionation decreases when the acidity increases in sulfuric acid solutions from 0.1 to 0.6 M [43]. We explain this observation by the formation of the less

reactive compound  $\text{IO}_2\text{H}_2^+$  with  $K_I$  about  $4 \text{ M}^{-1}$ . Using our values of the equilibrium constants  $K_B$  and  $K_C$ , we get

$$K_H^\circ = \frac{a_{\text{IO}_2\text{H}_2^+}^2}{a_{\text{IO}_3\text{H}}a_{\text{IOH}_2^+}a_{\text{H}^+}} = 10^{-7} \text{ M}^{-1}$$

and

$$\frac{[\text{IO}_2\text{H}_2^+]^2}{[\text{IO}_3\text{H}][\text{IOH}_2^+]} = K_H^\circ \times 10^{-H_0} \frac{\gamma_{\text{IO}_3\text{H}}\gamma_{\text{IOH}}}{\gamma_{\text{IO}_2\text{H}_2}^2}$$

where  $K_H^\circ \times 10^{-H_0} \sim 10^3$ . This result gives a theoretical explanation to the experimental observations of Noszticzus et al. [44].  $K_H^\circ \times 10^{-H_0}$  is large enough to obtain I(III) in concentrated sulfuric acid solutions but not very large so that a sufficient excess of  $\text{IO}_3\text{H}$  must be used to reduce the ratio I(I)/I(III). Iodine(III) solutions prepared by Noszticzus contained 6% or 3% iodine(I) for initial iodate/iodine mole ratios equal to 4 or 8. Although such calculations give only orders of magnitude, they are informative. In particular, they show that the concentration of sulfuric acid is critical. When it decreases, the value of  $10^{-H_0}$  decreases very quickly and the main product of the iodate–iodine reaction becomes I(I).

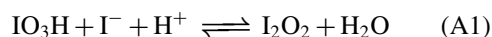
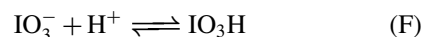
## CONCLUSIONS

To build models for complex systems, we must know a priori as many rate constants as possible. Sometimes it is possible to design specific experiments to measure them, sometimes it is not. In this paper, we use the criterion of thermodynamical consistency of reaction mechanism with the rate law and rate constant of reversible reactions in one direction to obtain the rate law and rate constants in the opposite direction. The values of the rate constants of reactions (B) and (C) at  $25^\circ\text{C}$  and their estimations at  $50^\circ\text{C}$  have consequences on the modeling of several systems mentioned in the introduction. We suggest that the formation of  $\text{IO}_2\text{H}_2^+$  cannot be neglected at acidities higher than 0.1 M. It explains the decrease of the rate of I(III) disproportionation when the acidity increases and is an essential part of the mechanism proposed in the appendix to explain the very high rate constant of reaction (+C).

## APPENDIX: MECHANISMS OF REACTIONS (B) AND (C)

In acidic nonbuffered solutions and iodide concentrations lower than  $10^{-7} \text{ M}$ , the first steps of the accepted

mechanism of the iodate–iodide reaction [33–36] are (F), (A1), and (A2). The sum of these reactions gives reaction (B). Under more general conditions, the rate law is complicated and the seemingly contradictory results are explained by the mechanism we have proposed [33].



Reaction (A1) could be split into  $\text{IO}_3\text{H} + \text{H}^+ \rightleftharpoons \text{IO}_3\text{H}_2^+$  and  $\text{IO}_3\text{H}_2^+ + \text{I}^- \rightleftharpoons \text{I}_2\text{O}_2 + \text{H}_2\text{O}$  without affecting our discussion. The intermediate  $\text{I}_2\text{O}_2$ , kinetically equivalent to its hydrated form  $\text{I}_2\text{O}_3\text{H}_2$ , has never been observed directly, but its existence is supported by such a large number of experimental observations that it would be very surprising to find another explanation. At the time scale of the global reaction, reaction (F) is a fast equilibrium and this mechanism gives the expected rate law

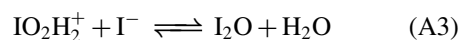
$$r_B = k_{+B}[\text{IO}_3^-][\text{I}^-][\text{H}^+]^2 - k_{-B}[\text{IO}_2\text{H}][\text{IOH}]$$

where

$$k_{+B} = \frac{K_F k_{+A1} k_{+A2}}{k_{-A1} + k_{+A2}} \quad k_{-B} = \frac{k_{-A1} k_{-A2}}{k_{-A1} + k_{+A2}}$$

Experiments performed under different conditions show that  $k_{-A1} \gg k_{+A2}$  [33], and the values of  $k_{+B}$  and  $k_{-B}$  are equal to  $K_F K_{A1} k_{A2}$  and  $k_{-A2}$ . Reaction (A2) is the rate-limiting step.

Reaction (C) is also not an elementary reaction, and we propose the following mechanism.



The existence of  $\text{I}_2\text{O}$  (a short form for the probably hydrated compound) is supported by our study of the IOH disproportionation [37] and is a key intermediate in our model of the Bray–Liebhafsky reaction [10–15]. At the time scale of the global reaction, reaction (I) is a fast equilibrium and this mechanism gives the rate law

$$r_C = k_{+C}[\text{IO}_2\text{H}][\text{I}^-][\text{H}^+] - k_{-C}[\text{IOH}]^2$$

where

$$k_{+C} = \frac{K_1 k_{+A3} k_{+A4}}{k_{-A3} + k_{+A4}} \quad k_{-C} = \frac{k_{-A3} k_{-A4}}{k_{-A3} + k_{+A4}}$$

In the main text, we show that the global constant  $k_{+C}$  is about  $1.9 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$ . This very large value can be explained if reaction (+A3) is diffusion controlled, provided that the other factors are large. We had assumed previously [10,37] that  $k_{+A4} \gg k_{-A3}$ . This inequality is further supported here as it maximizes the ratio  $k_{+A4}/(k_{-A3} + k_{+A4})$ . Then

$$k_{+C} = K_1 k_{+A3} \quad k_{-C} = \frac{k_{-A3}}{K_{A4}}$$

Taking  $k_{+A3} \leq 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for this kind of diffusion-controlled reaction [55,56] and  $K_1 \sim 4 \text{ M}^{-1}$  proposed in the main text, we explain the order of magnitude of  $k_{+C}$ . This mechanism also explains the decrease of the two rate constants  $k_{+C}$  and  $k_{-C}$  when the temperature increases.  $k_{+A3}$  should increase slowly with the temperature and if  $K_1$  decreases more quickly, their product  $k_{+C}$  decreases. Similarly, if  $K_{A4}$  increases more quickly than  $k_{-A3}$ ,  $k_{-C}$  decreases.

## BIBLIOGRAPHY

- Güntay, S. (Ed.). Proceedings of the Fourth CSNI Workshop on Iodine Chemistry in Reactor Safety, Würenlingen, Switzerland, June 1996.
- Wren, J. C.; Ball, J. M.; Glowa, G. A. Nucl Technol 2000, 129, 297.
- Wren, J. C.; Ball, J. M. Radiat Phys Chem 2001, 60, 577.
- Taghipour, F.; Evans, G. J Radiat Phys Chem 2002, 64, 203.
- Truesdale, V. W.; Canosa-Mas, C. E.; Luther, G. W., III. Mar Chem 1995, 51, 55.
- Bichsel, Y.; von Gunten, U. Water Res 2000, 34, 3197.
- Baker, A. R. Geophys Res Lett 2004, 31, L23S02/1–L23S02/4.
- Pechtl, S.; Schmitz, G.; von Glasow, R. Atmos Chem Phys 2007, 7, 1381.
- Furrow, S.D. In Oscillations and Traveling Waves in Chemical Systems, Field, R. J.; Burger, M. (Eds.); Wiley-Interscience: New York, 1985; pp. 171–192.
- Schmitz, G. J Chim Phys 1987, 84, 957.
- Kolar-Anić, Lj.; Schmitz, G. J Chem Soc, Faraday Trans 1992, 88, 2343.
- Kolar-Anić, Lj.; Čupić, Ž.; Anić, S.; Schmitz, G. J Chem Soc, Faraday Trans 1997, 93, 2147.
- Schmitz, G. Phys Chem Chem Phys 1999, 1, 4605.
- Schmitz, G. Phys Chem Chem Phys 2001, 3, 4741.
- Schmitz, G.; Kolar-Anić, Lj.; Anić, S.; Grozdić, T.; Vukojević, V. J Phys Chem A 2006, 110, 10361.
- Furrow, S. D. J Phys Chem 1995, 99, 11131.
- Vukojević, V.; Sorensen, P. G.; Hynne, F. J Phys Chem 1993, 97, 4091.
- Vukojević, V.; Sorensen, P. G.; Hynne, F. J Phys Chem 1996, 100, 17175.
- Kim, K.-R.; Lee, D. J.; Shin, K. J. J Chem Phys 2002, 117, 2710.
- Furrow, S. D.; Cervellati, R.; Amadori, G. J Phys Chem 2002, 106, 5841.
- Cervellati, R.; Hoener, K.; Furrow, S. D.; Mazzanti, F. Helv Chim Acta 2004, 87, 133.
- Cervellati, R.; Furrow, S. D. Inorg Chim Acta 2007, 360, 842.
- De Kepper, P.; Boissonade, J.; Epstein, I. R. J Phys Chem 1990, 94, 6525.
- Noszticzius, Z.; Qi, Outang, McCormick, W. D.; Swinney, H. L. J Am Chem Soc 1992, 114, 4290.
- Lengyel, I.; Li, J.; Kustin, K.; Epstein, I. R. J Am Chem Soc 1996, 118, 3708.
- Jowza, M.; Sattar, S.; Olsen, R. J. J Phys Chem A 2005, 109, 1873.
- De Kepper, P.; Epstein, I. R. J Am Chem Soc 1982, 104, 49.
- Gaspar, V.; Showalter, K. J Phys Chem 1990, 94, 4973.
- Edblom, E. C.; Gyorgyi, L.; Orban, M.; Epstein, I. R. J Am Chem Soc 1987, 109, 4876.
- Simoyi, R. H.; Manyonda, M.; Masere, J.; Mtambo, M.; Ncube, I.; Patel, H.; Epstein, I. R.; Kustin, K. J Phys Chem 1991, 95, 770.
- Rabai, G.; Kaminaga, A.; Hanazaki, I. J Phys Chem 1995, 99, 9795.
- Szalai, I.; De Kepper, P. Phys Chem Chem Phys 2006, 8, 1105.
- Schmitz, G. Phys Chem Chem Phys 1999, 1, 1909.
- Xie Yi; McDonald, M. R.; Margerum, D. W. Inorg Chem 1999, 38, 3938.
- Agreda B, J. A.; Field, R. J.; Lyons, N. J Phys Chem A 2000, 104, 5269.
- Schmitz, G. Phys Chem Chem Phys 2000, 2, 4041.
- Schmitz, G. Int J Chem Kinet 2004, 36, 480.
- Schmitz, G. J Chem Phys 2000, 112, 10714.
- Spitz, R. D.; Liebhafsky, H. A. J Electrochem Soc 1975, 122, 363.
- Palmer, D. A.; Ramette, R. W.; Mesmer, R. E. J Sol Chem 1984, 13, 685.
- Pitzer, K. S. Activity Coefficients in Electrolyte Solutions, 2nd ed.; CRC Press: Boca Raton, FL, 1991.
- Furuichi, R.; Liebhafsky, H. A. Bul Chem Soc Japan 1975, 48, 745.
- Furrow, S. J Phys Chem 1987, 91, 2129.
- Noszticzius, Z.; Noszticzius, E.; Schelly, Z. A. J Phys Chem 1983, 87, 510.
- Bard, A. J.; Parsons, R.; Jordan, J. Standard Potentials in Aqueous Solutions; IUPAC and Marcel Dekker: New York, 1985.
- Lide, D. R. (Editor-in Chief). Handbook of Chemistry and Physics, 85th ed.; CRC Press: Boca Raton, FL, 2004.

47. Dean, J. A. (Ed.). *Lange's Handbook of Chemistry*, 12th ed.; McGraw-Hill: New York, 1979.
48. Stanisavljev, D. *Ber Bunsen-Ges Phys Chem* 1997, 101, 1036.
49. de Barros Faria, R.; Epstein, I. R.; Kustin, K. *J Phys Chem* 1994, 98, 1363.
50. Ramette, R. W.; Palmer, D. A. *J Sol Chem* 1984, 13, 637.
51. Strong, L. E.; Pethybridge, A.D. *J Sol Chem* 1987, 16, 841.
52. Hammett, L. P. *Physical Organic Chemistry*; McGraw-Hill: New York, 1940.
53. Jorgensen, M. J.; Hartter, D. R. *J Am Chem Soc* 1963, 85, 878.
54. Giauque, W. G.; Hornung, E. W.; Kunzler, J. E.; Rubin, T. R. *J Am Chem Soc* 1960, 82, 62.
55. Jordan, P. C. *Chemical Kinetics and Transport*; Plenum Press: New York, 1979.
56. Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1995.