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Relationship among the Henry Law, Turkdogan Rule, and Two Extended Turkdogan Rules of Wang[†]

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In this paper, the Henry law (*Philos. Trans. R. Soc. London* **1803**, *93*, 29), the Turkdogan rule (*J. Iron Steel Inst., London* **1955**, *179*, 39, 155), and two extended Turkdogan rules of Wang (*Acta Metall. Sin. (Chin. Ed.)* **1980**, *16*, 195; *Ber. Bunsen−Ges.* **1998**, *102*, 1045) are presented in a unified way. Similar to the Henry law, which was first noted empirically from the solubility measurements of gases in water, the Turkdogan rule for carbon-saturated Fe-based liquid alloys can be extended to every kind of liquid and solid solutions such as organic mixtures, aqueous and nonaqueous electrolyte and nonelectrolyte solutions, liquid and solid alloys, molten salt mixtures, slags, and nonstoichiometric solid solutions, resulting in two extended Turkdogan rules of Wang. One solution, {B + C + ... + Z}, obeying the Henry law (or the related classically dilute solution model) may mix with many pure component A to form the solutions {A + B + C + ... + Z} following the first extended Turkdogan rule of Wang (or the related partial dilute solution model) or mix with much more nonideal solutions {A1 + A2 + ... + Aq} to form the solutions {A1 + A2 + ... + Aq + B + C + ... + Z} obeying the second extended Turkdogan rule of Wang (or the related dilute-like solution model). This would indicate that the Turkdogan rule and its extended forms are as important as the Henry law for multicomponent systems.

Introduction

Phase equilibria are required in the design of heterogeneous chemical reactions and separation processes. In almost all cases, the desired equilibria are for binary and higher-order systems rather than for pure components. On the other hand, there are many types of liquid and solid solutions in nature such as organic mixtures, aqueous and nonaqueous electrolyte and nonelectrolyte solutions, alloys, molten salt mixtures, slags, and nonstoichiometric solid solutions, which are important for chemistry, biology, geology, materials science, and engineering. Scientists working with different types of the solutions often use different concentration units, equations, and formalisms, which make it difficult for scientists in one field to understand or benefit from advances in other fields. It is therefore of considerable interest to search out general simple rules and to develop corresponding theoretical models with statistical information either for every kind of the binary and higher-order systems related to their pure components or for every kind of the ternary and higher-order systems related to their binary or higher-order subsystems.

Recently, we[1] presented the relationship among the Raoult law for every kind of solution {B + C + ... + Z}, the Zdanovskii−Stokes−Robinson (ZSR) rule[2,3] for isopiestic mixed electrolyte and nonelectrolyte aqueous solutions {water (A) + B + C + ... + Z}, the first extended ZSR rule of Wang[4−8] for every kind of solution {A + B + C + ... + Z} at constant activity of A, and the second extended ZSR rule of Wang[9] for every kind of solution {A1 + A2 + ... + Aq + B + C + ... + Z} at constant activities of A1, A2, ..., Aq, where there are zero interchange energies among B, C, ..., Z. The Henry law[10] and the related classically dilute solution model[11] for every kind of solution are as important as the Raoult law and the related classically ideal solution model in solution thermodynamics. In this study, we discuss the thermodynamic and statistical relationships among the Henry law for every kind of solution, {B + C + ... + Z}, the Turkdogan rule[12,13] for carbon-saturated Fe-based liquid alloys, {carbon(sat) (A) + iron (B) + alloying element (C) + ... + alloying element (Z)}, and two extended Turkdogan rules of Wang[4−7,9] for every kind of solution, {A + B + C + ... + Z}, at constant activity of A, and {A1 + A2 + ... + Aq + B + C + ... + Z} at constant activities of A1, A2, ..., Aq, respectively, which all hold well at constant temperature and pressure.

Henry Law and the Model

The Henry law was first proposed empirically for the solubility measurements of sparingly soluble gases in water, where the solute species is the same in the solution as in the gas, and may be expressed as

$$p_j = h_j x_j \tag{1}$$

where $j \in$ (C, D, ⋯, Z) denotes the solutes (and B denotes the solvent) in the solution {water (B) + solute (C) + solute (D) + ... + solute (Z)}; p_j and x_j are the pressure and mole fraction of solute j; and h_j is the Henry law constant of solute j. Although scientists often have different opinions on solution models particularly at the liquid state, one of the first successes for understanding different kinds of the solutions in a unified way would be the development of the classically dilute solution model, which is based on the Henry law and derived from a quasi-chemical treatment.[11] The Henry law is now rewritten as

$$a_j = k_j x_j \tag{2}$$

or it equals within $0 \le x_j \le x_j^*$ for every kind of solution {B + C + ... + Z} with nonzero interchange energies between solvent

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B and every solute C, D, ..., Z, where a_j is the activity of solute j and x_j^* denotes the boundary value of x_j, at which eq 2 holds well. Since the classically dilute solution model may also be followed by the solutions where the solute species in the solution is different from that in the gas (or other phases), the classically dilute solution model equations may generally be given by

$$V_m = x_B V^{\circ}_{m,B} + \sum_j x_j V^{\infty}_{m,j} \tag{3a}$$

$$S_m = (x_B S^{\circ}_{m,B} + \sum_j x_j S^{\infty}_{m,j}) - R \sum_i x_i \ln z_i \tag{3b}$$

$$H_m = x_B H^{\circ}_{m,B} + \sum_j x_j H^{\infty}_{m,j} \tag{3c}$$

$$G_m = (x_B G^{\circ}_{m,B} + \sum_j x_j G^{\infty}_{m,j}) + RT \sum_i x_i \ln z_i \tag{3d}$$

$$\mu_B = \mu_B^{\circ} + RT \ln z_B \tag{3e}$$

$$\mu_j = \mu_j^{\infty} + RT \ln z_j \tag{3f}$$

$$a_B = z_B \tag{3g}$$

$$a_j = k_j z_j \tag{3h}$$

over $x_j < 0.01$, roughly speaking, where $i \in$ (B, C, ⋯, Z) denotes components in the solution {B + C + ... + Z}; V_m is molar volume; S_m is molar entropy; H_m is molar enthalpy; G_m is molar Gibbs energy; μ_i is the chemical potential of component i; the superscript ° combined with the subscript B denotes a property of pure component B, so that $V^{\circ}_{m,B}$, $S^{\circ}_{m,B}$, $H^{\circ}_{m,B}$, and $G^{\circ}_{m,B}$ are molar quantities of pure B and μ_B° is the chemical potential of pure B; the superscript ∞ combined with the subscript j denotes a property of the pure component j at a hypothetical state obtained by extrapolating eqs 2 and 3 to $x_j = 1$, so that $V^{\infty}_{m,j}$, $S^{\infty}_{m,j}$, $H^{\infty}_{m,j}$, $G^{\infty}_{m,j}$, and μ_j^{∞} are the properties of pure j at the hypothetical state; R is gas constant; T is temperature; and z_i is a composition variable of component i, such as $z_i = [\nu_i^+ n_i/(\nu_B^+ n_B + \nu_C^+ n_C)]^{\nu_i^+}[\nu_i^- n_i/(\nu_B^- n_B + \nu_C^- n_C)]^{\nu_i^-}$ for a molten salt mixture {B + C} with no common ion,[1] $z_i = [\nu_i^- n_i/(\nu_B^- n_B + \nu_C^- n_C)]^{\nu_i^-}$ for a molten salt mixture {B + C} with the same cation,[1] $z_i = [\nu_i^+ n_i/(\nu_B^+ n_B + \nu_C^+ n_C)]^{\nu_i^+}$ for a molten salt mixture {B + C} with the same anion,[1] $z_i = [\nu_i n_i/(\nu_B n_B + \nu_C n_C)]^{\nu_i}$ for an alloy {B + C} with dissociation reactions such as $N_2(g) = 2N$(in metals), and $z_i = [n_i/(n_B + n_C)] = x_i$ for a nondissociation and nonpolymerization system {B + C}. Here, n_i is mole number of component i; ν_i is the stoichiometric coefficient of component i in the dissociation or ionization reactions, and ν_i^+ and ν_i^- are the stoichiometric coefficients for the cation and anion of component i in ionization reactions. Equation 3 connects the properties of the solution {B + C + ... + Z} with those of its pure component B and those of its pure components C, D, ..., Z at their hypothetical state.

One pair of dissimilar components, B and C, which may form the classically dilute solution {B + C}, may mix with various pure components A or various solutions {A1 + A2 + ... + Aq} to form numbers of the real solutions, {A + B + C} or {A1 + A2 + ... + Aq + B + C}. Therefore, the real solutions {A + B + C + ... + Z} and {A1 + A2 + ... + Aq + B + C + ... + Z} formed from the classically dilute solution {B + C + ... + Z} are very interesting for both theorists and experimentalists.

Turkdogan Rule

In 1955, Turkdogan and his co-workers reported the linear relations for carbon-saturated Fe-based liquid alloys: $\Delta x_{carbon} \equiv x_{carbon} - x_{carbon}^{iron} = -0.84 x_{phosphorus}$ for {carbon(sat) (A) + iron (B) + phosphorus (C)} at about (1290 to 1575) °C and within about $0 \le x_{phosphorus} \le 0.045$,[12] $\Delta x_{carbon} = -0.71 x_{silicon}$ for {carbon(sat) (A) + iron (B) + silicon (C)} at about (1290 to 1690) °C and within about $0 \le x_{silicon} \le 0.08$,[12] $\Delta x_{carbon} = 0.1 x_{manganese}$ for {carbon(sat) (A) + iron (B) + manganese (C)} at about (1290 to 1690) °C and within about $0 \le x_{manganese} \approx 0.6$,[12] and $\Delta x_{carbon} = -x_{sulfur}$ for {carbon(sat) (A) + iron (B) + sulfur (C)} at about (1200 to 1500) °C and within about $0 \le x_{sulfur} \le 0.01$;[13] where x_{carbon} is the carbon solubility (atomic fraction) and x_{carbon}^{iron} is the carbon solubility in the binary melts {carbon(sat) (A) + iron (B)}.

Wang[4−7] called these relations the Turkdogan rule and rewrote them as

$$\Delta x_{carbon} \equiv x_{carbon} - x_{carbon}^{iron} = \sum_j b_j x_j \tag{4}$$

for the carbon-saturated Fe-based liquid alloys {carbon(sat) (A) + iron (B) + alloying element (C) + ... + alloying element (Z)} within $0 \le x_j \le x_j^* < 1$, where x_j denotes the atomic fraction of the alloying element j and x_j^* denotes the boundary concentration of component j, at which eq 4 holds well. Similar linear solubility phenomena were also found for carbon-saturated Co- and Ni-based liquid alloys.[14]

First Extended Turkdogan Rule of Wang and the Model

Wang[4−7] found that eq 4 can be rewritten as

$$\tau_A = (\tau_B/\tau_B^{1\circ})\tau_A^{1\circ,B} + \sum_j (\tau_j/\tau_j^{1\infty})\tau_A^{1\infty,j} = \tau_A^{1\circ,B} + \sum_j b_j' \tau_j \tag{5a}$$

$$(\tau_B/\tau_B^{1\circ}) + \sum_j (\tau_j/\tau_j^{1\infty}) = 1 \tag{5b}$$

$$\omega = (x_B/\sum_k x_k)\omega^{1\circ,B} + \sum_j (x_j/\sum_k x_k)\omega^{1\infty,j} \tag{5c}$$

within $0 \le (\tau_j/\tau_j^{1\infty}) \le (\tau_j^*/\tau_j^{1\infty}) < 1$ (or $0 \le (\tau_j/\sum_k \tau_k) \le (\tau_j^*/\sum_k \tau_k^*) < 1$) and can be extended to every kind of the solution {A + B + C + ... + Z} with nonzero interchange energy between B and each C, D, ..., Z at constant activity (or chemical potential, or partial Gibbs free energy) of A, where $k \in$ (B, C, ⋯, Z); hence, $\sum_i (x_i/\sum_k x_k) = 1$; τ_i may denote either molality m_i, atomic or mole fraction x_i, or mass fraction w_i of component i; ω may denote the solubility of solute A in 1 mol of the mixed solvent [B + C + ... + Z] or the oxygen-to-metal ratio (O/M) for nonstoichiometric solid mixed-oxide solutions {oxygen (A) + metal (B) + metal (C) + ... + metal (Z)}; the superscript 1°,B (or the superscript 1° combined with the subscript B) denotes a property of the binary subsystem {A + B} so that $\tau_A^{1\circ,B}$ and $\tau_B^{1\circ}$ are the concentrations of components A and B, respectively, in the binary subsystem {A + B}, and $\omega^{1\circ,B}$ is the property of the binary subsystem {A + B}; the superscript 1∞,j (or the superscript 1∞ combined with the subscript j) denotes a property of the binary subsystem {A + j} at the hypothetical state obtained by extrapolating eq 5 to $(\tau_j/\tau_j^{1\infty}) = 1$, so that $\tau_A^{1\infty,j}$ and $\tau_j^{1\infty}$ are the concentrations of components A and j, respectively, in the binary subsystem {A + j} at the hypothetical state, and $\omega^{1\infty,j}$ is the property of the hypothetical binary subsystem {A + j}; and τ_j^* is the boundary concentration of component j, at which eq 5 holds well. Moreover, Wang[4] noted that eq 5 may hold in a narrower concentration range if the interchange energies are larger between B and every j or in a wider concentration range if the interchange energies are smaller between B and every *j*. In addition, similar to the first extended ZSR rule of Wang,[1,4,5] eq 5 may also be valid at a constant other partial molar quantity,[4,5] for example, the {water (A) + $CaCl_2$ (B) + HCl (C)} system at constant partial molar enthalpy of water. It would be therefore that eq 5 might be called the first extended Turkdogan rule of Wang, similar to the first extended ZSR rule of Wang shown in ref 1. Chinese scientists called eq 5 the Wang Zhichang's linear concentration rule at constant partial molar quantity[15] and experimentally verified it by the solubility measurements of metals in nonferrous liquid alloys.[16]

On the basis of eq 5 and its thermodynamic aspect,[5] Wang[6,7] developed a partial dilute solution model from a modified quasi-chemical treatment for every kind of the solution {A + B + C + ... + Z} with nonzero interchange energy between B and each C, D, ..., Z at constant activity of A, which may generally be given by eqs 5 and 6:

$$V_m = (x_B/x_B^{1\circ})V_{m,B}^{1\circ} + \sum_j (x_j/x_j^{1\infty})V_{m,j}^{1\infty} \tag{6a}$$

$$S_m = \{(x_B/x_B^{1\circ})S_{m,B}^{1\circ} + \sum_j (x_j/x_j^{1\infty})S_{m,j}^{1\infty}\} - R\sum_i x_i \ln z_i \tag{6b}$$

$$H_m = (x_B/x_B^{1\circ})H_{m,B}^{1\circ} + \sum_j (x_j/x_j^{1\infty})H_{m,j}^{1\infty} \tag{6c}$$

$$G_m = \{(x_B/x_B^{1\circ})G_{m,B}^{1\circ} + \sum_j (x_j/x_j^{1\infty})G_{m,j}^{1\infty}\} + RT\sum_i x_i \ln z_i \tag{6d}$$

$$\mu_B = \mu_B^{1\circ} + RT \ln z_B \tag{6e}$$

$$\mu_j = \mu_j^{1\infty} + RT \ln z_j \tag{6f}$$

$$(a_B/a_B^{1\circ}) = z_B \tag{6g}$$

$$(a_j/a_j^{1\infty}) = z_j \tag{6h}$$

over $(x_j/\sum_k x_k) < 0.01$, roughly speaking, where $V_{m,B}^{1\circ}$, $S_{m,B}^{1\circ}$, $H_{m,B}^{1\circ}$, and $G_{m,B}^{1\circ}$ are molar quantities of the binary subsystem {A + B}; $\mu_B^{1\circ}$, $a_B^{1\circ}$, and $x_B^{1\circ}$ are chemical potential, activity, and mole fraction of component B in the binary subsystem {A + B}; $V_{m,j}^{1\infty}$, $S_{m,j}^{1\infty}$, $H_{m,j}^{1\infty}$, and $G_{m,j}^{1\infty}$ are molar quantities of the binary subsystem {A + *j*} at the hypothetical state; and $\mu_j^{1\infty}$, $a_j^{1\infty}$, and $x_j^{1\infty}$ are the properties of component *j* in the binary subsystem {A + *j*} at the hypothetical state. Here, the composition variable z_i of component *i* is given by $z_i = [n_i/(n_B + n_C)]$ for a nondissociation and nonpolymerization system {A + B + C} but by different formulas for different kinds of ionic solutions {A + B + C}, for example, $z_i = [\nu_i^+ n_i/(\nu_B^+ n_B + \nu_C^+ n_C)]^{\nu_i^+}$ for molten salt mixtures with the same anion[5−9] and $z_i = [\nu_i n_i/(\nu_B n_B + \nu_C n_C)]^{\nu_i}/[\nu_i^- n_i/(\nu_B^- n_B + \nu_C^- n_C)]^{\nu_i^-}$ for aqueous solutions with the same anion.[5−9] Both eqs 5 and 6 connect the properties of the solution {A + B + C + ... + Z} with those of its binary subsystem {A + B} and those of its binary subsystems {A + *j*} at their hypothetical state under the condition at constant activity of A. Equation 5 also indicates the identity of the isoactivity line of A and the mixing line among the binary subsystems within the concentration ranges. A comparison of eq 6 with eq 3 shows that the partial dilute solution model may reduce to the classically dilute solution model at $x_A = 0$ and that a pure component A + a classically dilute solution {B + C + ... + Z} = a partial dilute solution {A + B + C + ... + Z}. The Henry law or the classically dilute solution model for {B + C + ... + Z} may be derived when the first extended Turkdogan rule of Wang or the partial dilute solution model for {A + B + C + ... + Z} holds well from infinite dilution of B, C, ..., Z, where $a_A = 1$ and all $a_i = 0$, to infinite dilution of A, where $a_A = 0$.

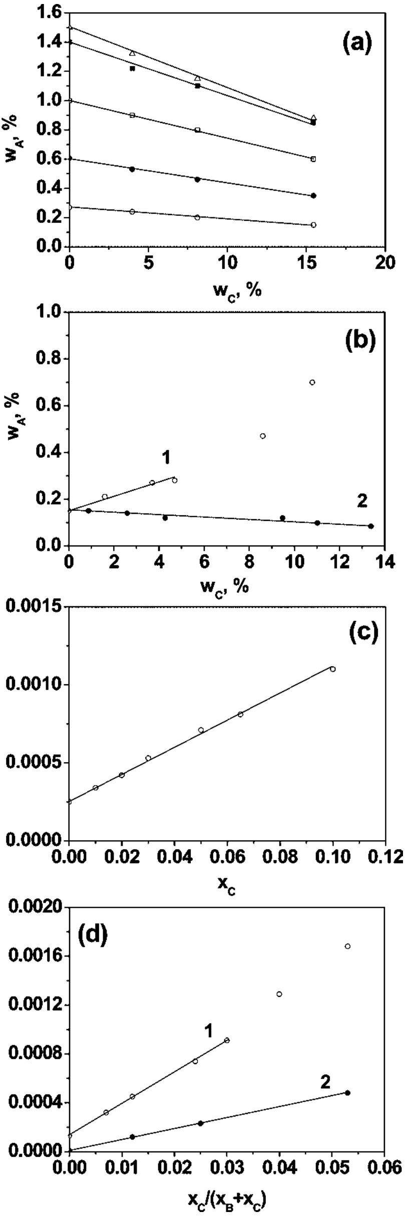

Figure 1. Isoactivity concentrations for different kinds of solid and liquid solutions: (a) isoactivity lines of carbon in the solid solution {carbon (A) + iron (B) + nickel (C)}[17] at 1000 °C; (b) line 1 for the melts {calcium(sat) (A) + manganese (B) + aluminum (C)}[16] and line 2 for the melts {calcium(sat) (A) + manganese (B) + chromium (C)}[16] at 1350 °C; (c) the melts {cadmium(sat) (A) + NaCl−KCl (B) + $CdCl_2$ (C)}[18] at 700 °C; and (d) line 1 for {*o*-nitroaniline(sat) (A) + water (B) + DMF (C)}[19] and line 2 for {*p*-chlorobenzoic acid(sat) (A) + water (B) + DMF (C)}[19] at 303 K. The solid lines are given by eq 5a in a, b, and c and by eq 5c in d.

Figure 1a shows that eq 5 fits the isoactivity lines of carbon very well for the solid alloys {carbon (A) + iron (B) + nickel (C)}[17] at 1000 °C, within $0 \le w_C \le 0.15$, and under the carbon activity values of $a_{carbon} = 0.0138$, 0.0352, 0.0676, 0.115, and 0.141, respectively. Figure 1, parts b−d, shows that eq 5 can fit the solubility measurements of calcium in the liquid nonferrous alloys {calcium(sat) (A) + manganese (B) + aluminum (C)}[16] within about $0 \le w_C \le 0.047$ and {calcium(sat) (A) +

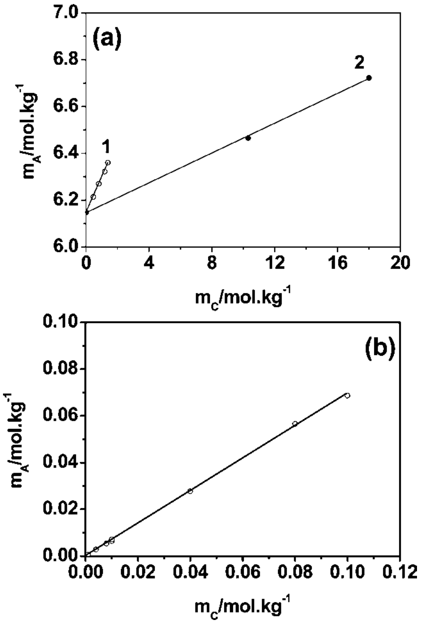

Figure 2. Isoactivity concentrations for aqueous solutions under normal or superscript conditions: (a) line 1 for {NaCl(sat) (A) + water (B) + mannitol (C)}[20] up to mannitol saturation and line 2 {NaCl(sat) (A) + water (B) + urea (C)}[21] at 25 °C and (b) for {Al_2O_3(sat) (A) + water (B) + KOH (C)}[22] at 400 °C and under 1 kbar. The solid lines are given by eq 5a.

manganese (B) + chromium (C)}[16] within about $0 \le w_C \le 0.134$ at 1350 °C, cadmium in the metal−salt melts {cadmium(sat) (A) + NaCl−KCl (B) + $CdCl_2$ (C)}[18] at 700 °C within about $0 \le [x_C/(x_B + x_C)] \le 0.1$, and chlorobenzoic acid and nitroaniline in the mixed solvent systems {*p*-chlorobenzoic acid(sat) (A) + water (B) + DMF (C)}[19] and {*o*-nitroaniline(sat) (A) + water (B) + DMF (C)}[19] at 303 K within about $0 \le [x_C/(x_B + x_C)] \le 0.03$, respectively, where DMF = *N*,*N*-dimethylformamide. Figure 2 shows that eq 5 can also fit the solubility measurements in aqueous solutions under both the normal and the supercritical conditions: {NaCl(sat) (A) + water (B) + mannitol (C)}[20] to mannitol saturation, {NaCl(sat) (A) + water (B) + urea (C)}[21] to a high concentration of urea at 25 °C, and {Al_2O_3(sat) (A) + water (B) + KOH (C)}[22] at 400 °C and under 1 kbar. In addition, in ref 23, Pabalan and Pitzer presented more than twenty figures for mineral solubilities in the ternary aqueous solutions {saturated electrolyte (A) + water (B) + unsaturated electrolyte (C)}, which also fit eq 5a well, at least in the low concentration ranges of component C.

More importantly, Rard and Platford[24] have pointed out the high accuracy of room temperature isopiestic determinations for aqueous solutions above 0.1 mol·kg^{-1}. Figure 3 shows that eq 5b can fit very closely the room temperature isopiestic measurements for {water (A) + KCl (B) + mannitol (C)}[25] and {water (A) + NaCl (B) + mannitol (C)}[20] up to the concentrations close to the saturation molality of mannitol, 1.185 mol·kg^{-1}. Figure 3 also shows that eq 5b can fit the room temperature isopiestic behavior of {water (A) + NaPAA (B) + PVP (C)}[26] very well, where the weight average degree of polymerization was 640 for NaPAA (sodium polyacrylate) and the molecular weight was 24 500 for PVP (polyvinylpyrrolidone).

Furthermore, Robinson and Stokes[25] have derived the equations for activity coefficients of KCl and mannitol in {water (A) + KCl (B) + mannitol (C)} from isopiestic measurements at 298.15 K on the basis of a cross-differential assumption. In Figure 4, the activity coefficients of KCl and mannitol in {water (A) + KCl (B) + mannitol (C)} calculated from their equations are used to check eqs 6g and 6h. The agreement is very good.

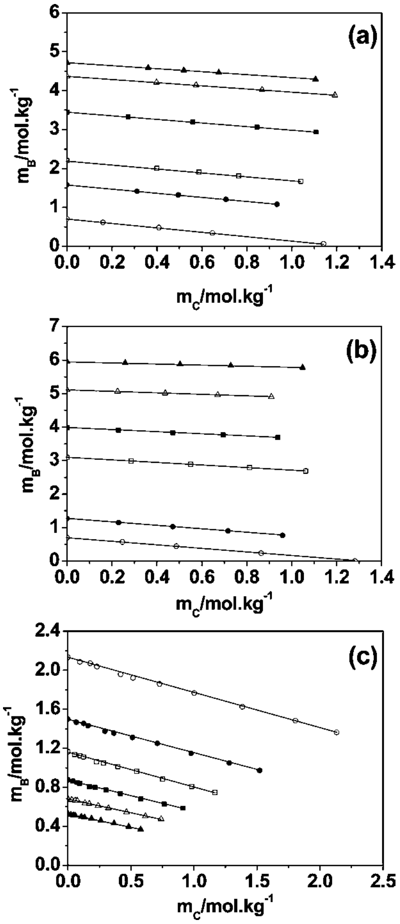

Figure 3. Isopiestic concentrations for (a) {water (A) + KCl (B) + mannitol (C)},[25] (b) {water (A) + NaCl (B) + mannitol (C)},[20] and (c) {water (A) + NaPAA (B) + PVP (C)}[26] at 25 °C, at which temperature the solubility of mannitol in {water (A) + mannitol (C)} is 1.185 mol·kg^{-1}.[20,25] The solid lines are given by eq 5b.

In addition, Petot et al.[27] experimentally determined the activities of iron in the {carbon(sat) (A) + iron (B) + manganese (C)} melts at 1320 °C, which also reasonably fit eq 6g within about $0.95 \le z_B \le 1$ (or $0 \le z_C \le 0.05$) as shown in Figure 5.

Second Extended Turkdogan Rule of Wang and the Model

Wang[9] also developed a dilute-like solution model from another modified quasi-chemical treatment for every kind of the solution {A1 + A2 + ... + A*q* + B + C + ... + Z} with nonzero interchange energies between B and each C, D, ..., Z at constant activities of A1, A2, ..., A*q* with the main model equations being:

$$\tau_\beta = (\tau_B/\tau_B^{q\circ})\tau_\beta^{q\circ,B} + \sum_j (\tau_j/\tau_j^{q\infty})\tau_\beta^{q\infty,j} = \tau_\beta^{q\circ,B} + \sum_j b_j''\tau_j \tag{7a}$$

$$(\tau_B/\tau_B^{q\circ}) + \sum_j (\tau_j/\tau_j^{q\infty}) = 1 \tag{7b}$$

$$\{(m_B/m_\beta)/(m_B^{q\circ}/m_\beta^{q\circ,B})\} + \sum_j \{(m_j/m_\beta)/(m_j^{q\infty}/m_\beta^{q\infty,j})\} = 1 \tag{7c}$$

$$s_\beta = (x_B/\sum_k x_k)s_\beta^{q\circ,B} + \sum_j (x_j/\sum_k x_k)s_\beta^{q\infty,j} \tag{7d}$$

$$V_m = (x_B/x_B^{q\circ})V_{m,B}^{q\circ} + \sum_j (x_j/x_j^{q\infty})V_{m,j}^{q\infty} \tag{8a}$$

$$S_{\mathrm{m}} = \{(x_{\mathrm{B}}/x_{\mathrm{B}}^{q\circ})S_{\mathrm{m,B}}^{q\circ} + \sum_j (x_j/x_j^{q\infty})S_{\mathrm{m},j}^{q\infty}\} - R\sum_i x_i \ln z_i \tag{8b}$$

$$H_{\mathrm{m}} = (x_{\mathrm{B}}/x_{\mathrm{B}}^{q\circ})H_{\mathrm{m,B}}^{q\circ} + \sum_j (x_j/x_j^{q\infty})H_{\mathrm{m},j}^{q\infty} \tag{8c}$$

$$G_{\mathrm{m}} = \{(x_{\mathrm{B}}/x_{\mathrm{B}}^{q\circ})G_{\mathrm{m,B}}^{q\circ} + \sum_j (x_j/x_j^{q\infty})G_{\mathrm{m},j}^{q\infty}\} + RT\sum_i x_i \ln z_i \tag{8d}$$

$$\mu_{\mathrm{B}} = \mu_{\mathrm{B}}^{q\circ} + RT \ln z_{\mathrm{B}} \tag{8e}$$

$$\mu_j = \mu_j^{q\infty} + RT \ln z_j \tag{8f}$$

$$(a_{\mathrm{B}}/a_{\mathrm{B}}^{q\circ}) = z_{\mathrm{B}} \tag{8g}$$

$$(a_j/a_j^{q\infty}) = z_j \tag{8h}$$

over $(x_j/\sum_k x_k) < 0.01$ roughly speaking, where $\beta \in$ (A1, A2, $\cdots$, Aq) denotes components having constant activities in the solution {A1 + A2 + ... + Aq + B + C + ... + Z} and its (q + 1)-component subsystem {A1 + A2 + ... + Aq + B} and its (q + 1)-component subsystems {A1 + A2 + ... + Aq + j} at the hypothetical state obtained by extrapolating eqs 7 and 8 to $(\tau_j/\tau_j^{q\infty}) = 1$; $s_\beta[= n_\beta/(n_{\mathrm{B}} + n_{\mathrm{C}} + \cdots + n_{\mathrm{Z}})]$ denotes the solubility of solute β in the solution {A1 + A2 + ... + Aq + B + C + ... + Z} formed from a solute mixture [A1 + A2 + ... + Aq] and a solvent mixture [B + C + ... + Z]; the superscript $q°$,B (or the superscript $q°$ combined with the subscript B) denotes a property of the (q + 1)-component subsystem {A1 + A2 + ... + Aq + B}, and the superscript $q\infty$,j (or the superscript $q\infty$ combined with the subscript j) denotes a property of the (q + 1)-component subsystems {A1 + A2 + ... + Aq + j} at the hypothetical state, so that $V_{\mathrm{m,B}}^{q°}$, $S_{\mathrm{m,B}}^{q°}$, $H_{\mathrm{m,B}}^{q°}$, and $G_{\mathrm{m,B}}^{q°}$ are molar quantities of the subsystem {A1 + A2 + ... + Aq + B}; $\mu_{\mathrm{B}}^{q°}$ and $a_{\mathrm{B}}^{q°}$ are the chemical potential and activity of component B in the subsystem {A1 + A2 + ... + Aq + B}; $x_{\mathrm{B}}^{q°}$, $m_{\mathrm{B}}^{q°}$, and $\tau_{\mathrm{B}}^{q°}$ are the concentrations of component B in the subsystem {A1 + A2 + ... + Aq + B}; $\tau_\beta^{q°,\mathrm{B}}$ and $m_\beta^{q°,\mathrm{B}}$ are the concentrations of component β in the subsystem {A1 + A2 + ... + Aq + B}; $s_\beta^{q°,\mathrm{B}}$ denotes the solubility of solute β in the subsystem {A1 + A2 + ... + Aq + B}; $V_{\mathrm{m},j}^{q\infty}$, $S_{\mathrm{m},j}^{q\infty}$, $H_{\mathrm{m},j}^{q\infty}$, and $G_{\mathrm{m},j}^{q\infty}$ are the properties of the (q + 1)-component subsystems {A1 + A2 + ... + Aq + j} at the hypothetical state; and $\mu_j^{q\infty}$, $a_j^{q\infty}$, $\tau_j^{q\infty}$, $m_j^{q\infty}$, and $x_j^{q\infty}$ are the properties of component j and $\tau_\beta^{q\infty,j}$, $m_\beta^{q\infty,j}$, and $s_\beta^{q\infty,j}$ are the properties of component β in the (q + 1)-component subsystems {A1 + A2 + ... + Aq + j} at the hypothetical state. In the special case that τ denotes molality and β = water, eq 7c reduces to eq 7b due to $m_\beta = m_\beta^{q°,\mathrm{B}} = m_\beta^{q\infty,j} = 55.506\ \mathrm{mol \cdot kg^{-1}}$. It would be therefore that eq 7 might be called the second extended Turkdogan rule of Wang.

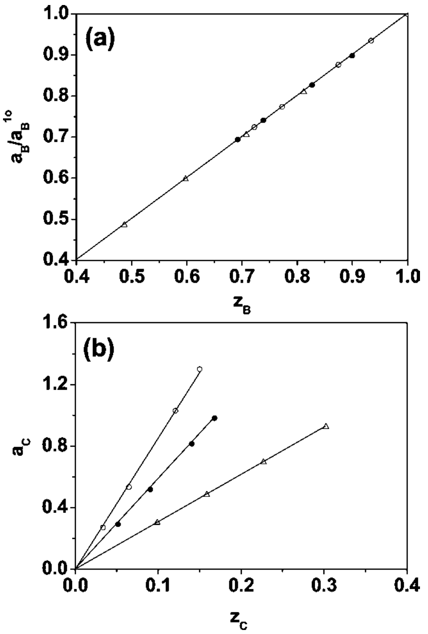

Figure 4. Activities for (a) KCl and (b) mannitol in {water (A) + KCl (B) + mannitol (C)} at 25 °C[25] along the isopiestic lines of water at a_{A} = 0.8529, 0.9036, and 0.9493, respectively, and with $z_{\mathrm{B}} = [2m_{\mathrm{B}}/(2m_{\mathrm{B}} + m_{\mathrm{C}})]^2$ and $z_{\mathrm{C}} = m_{\mathrm{C}}/(2m_{\mathrm{B}} + m_{\mathrm{C}})$. The open triangles at a_{A} = 0.8529, solid circles at a_{A} = 0.9036, and open circles at a_{A} = 0.9493 were calculated by eqs 2 and 3 in ref 25 for activity coefficients of mannitol and KCl, respectively, together with the basic equations $a_{\mathrm{B}} = m_{\mathrm{B}}^2\gamma_{\mathrm{B}}^2$ and $a_{\mathrm{C}} = m_{\mathrm{C}}\gamma_{\mathrm{C}}$, where γ is the activity coefficient. The solid lines are given by eq 6g for KCl in Figure 4a and by eq 6h for mannitol in Figure 4b.

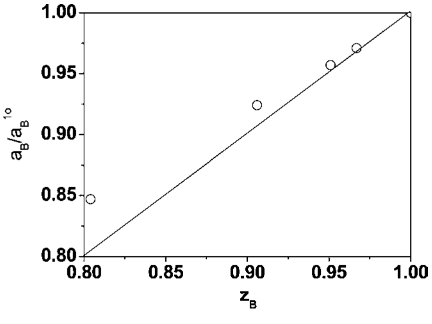

Figure 5. Activities for iron in {carbon(sat) (A) + iron (B) + manganese (C)} at 1773 K. The solid line is given by eq 6g.

Equations 7 and 8 connect the properties of the solution {A1 + A2 + ... + Aq + B + C + ... + Z} with those of its (q + 1)-component subsystem {A1 + A2 + ... + Aq + B} and those of its (q + 1)-component subsystems {A1 + A2 + ... + Aq + j} at the hypothetical state under the condition at constant activities of A1, A2, ..., Aq. Equation 7 also indicates the identity of the common isoactivity line of A1, A2, ..., Aq and the mixing line among the (q + 1)-component subsystems within the concentration ranges. Comparison of eqs 7 and 8 with eqs 5 and 6 and with eqs 2 and 3 shows that the dilute-like solution model reduces to the partial dilute solution model at $q = 1$ (i.e., A1 = A and $x_{\mathrm{A2}} = x_{\mathrm{A3}} = \cdots = x_{\mathrm{A}q} = 0$) and to the classically dilute solution model at $q = 0$ (i.e., $x_{\mathrm{A1}} = x_{\mathrm{A2}} = \cdots = x_{\mathrm{A}q} = 0$) and that a classically nonideal solution {A1 + A2 + ... + Aq} + a classically dilute solution {B + C + ... + Z} = a dilute-like solution {A1 + A2 + ... + Aq + B + C + ... + Z}. The Henry law or the classically dilute solution model for {B + C + ... + Z} may be derived when the second extended Turkdogan rule of Wang or the dilute-like solution model holds well from infinite dilution of B, C, ..., Z, where all $a_i = 0$, to infinite dilution of A1, A2, ..., Aq, where all $a_\beta = 0$, for {A1 + A2 + ... + Aq + B + C + ... + Z}.

Equations 7 and 8 may be checked either by the isopiestic measurements for the aqueous solutions {water (A1) + A2 + ... + Aq + B + C + ... + Z} with one or more saturated solutes or volatile alcohols denoted by A2, A3, ..., Aq and with two or more unsaturated solutes denoted by B, C, ..., Z or by the joint solubility measurements of the solute mixtures [A1 + A2 + ... + Aq] in the mixed solvents [B + C + ... + Z]. For example, Wang[9] has reported the isopiestic measurements for {water (A1) + mannitol(sat) (A2) + KCl (B) + $\mathrm{CdCl_2}$ (C)} within $0 \le [m_{\mathrm{C}}/(m_{\mathrm{B}} + m_{\mathrm{C}})] \le 0.1002$, for {water (A1) + mannitol(sat) (A2) + $\mathrm{CdCl_2}$ (B) + KCl (C)} within $0 \le [m_{\mathrm{C}}/(m_{\mathrm{B}} + m_{\mathrm{C}})] \le 0.0737$, for {water (A1) + NaCl(sat) (A2) + urea (B) + sucrose (C)} within $0 \leq [m_C/(m_B + m_C)] \leq 0.0543$, and for {water (A1) + NaCl(sat) (A2) + sucrose (B) + urea (C)} within $0 \leq [m_C/(m_B + m_C)] \leq 0.0552$, where $CdCl_2$ is a strong complex former with KCl and the unsaturated ternary subsystem {water (A) + sucrose (B) + urea (C)} significantly deviates from the ZSR rule.[3] All of the results closely fit eqs 7b and 7c.

Discussion

The Henry law was first discovered empirically for solubility measurements of gases in water, while the Turkdogan rule was discovered empirically for solubility measurements of carbon in Fe-based liquid alloys. The classically dilute solution model derived from a quasi-chemical treatment makes the Henry law valid for every kind of the liquid and solid solutions {B + C + ... + Z} such as organic mixtures, aqueous and nonaqueous electrolyte and nonelectrolyte solutions, alloys, molten salt mixtures, slags, and nonstoichiometric solid solutions. The partial dilute solution model and dilute-like solution model derived from modified quasi-chemical treatments result in two extended Turkdogan rules of Wang, which are valid for every kind of the liquid and solid solutions {A + B + C + ... + Z} at constant activity of A and for every kind of the liquid and solid solutions {A1 + A2 + ... + Aq + B + C + ... + Z} at constant activities of A1, A2, ..., Aq, respectively. The classically dilute solution model, partial dilute solution model, and dilute-like solution model are all valid over $(x_j/\sum_k x_k) < 0.01$, roughly speaking, for the systems with nonzero interchange energies between B and each C, D, ..., Z. The relationship among the three models might be given by "a pure component A + a classically dilute solution {B + C + ... + Z} = a partial dilute solution {A + B + C + ... + Z}" and "a classically nonideal solution {A1 + A2 + ... + Aq} + a classically dilute solution {B + C + ... + Z} = a dilute-like solution {A1 + A2 + ... + Aq + B + C + ... + Z}". In other words, in the case that {B + C + ... + Z} follows the classically dilute solution model, the partial dilute solution model is valid over the whole range of the activity of A for the classically nonideal solution {A + B + C + ... + Z} and the dilute-like solution model over the whole range of the activities of A1, A2, ..., Aq for the classically nonideal solution {A1 + A2 + ... + Aq + B + C + ... + Z}. Therefore, after extension, the Turkdogan rule would be as important as the Henry law in multicomponent systems. In the case that there are stronger interactions or larger interchange energies between B and each C, D, ..., Z, the Henry law for {B + C + ... + Z} and two extended Turkdogan rules of Wang for {A + B + C + ... + Z} and {A1 + A2 + ... + Aq + B + C + ... + Z}, respectively, and their models might be valid only in a narrower concentration range, that is, $0 \leq x_j \leq x_j^* \ll 1$. In another case where there are weaker interactions or smaller interchange energies between B and each C, D, ..., Z, these rules and models might be valid in a wider concentration range, that is, $0 \leq x_j \leq x_j^* < 1$ with a larger value of x_j^*. In the third case that there are zero interchange energies between B and each C, D, ..., Z, the Henry law reduces to Raoult law and the two extended Turkdogan rules of Wang reduce to the two extended ZSR rules of Wang.[1]

Furthermore, at constant activities of A1, A2, ..., Aq, the general concentration relation may be given by[9]

$$x_\beta = (x_B/x_B^{q\circ})x_\beta^{q\circ,B} + (x_C/x_C^{q\circ})x_\beta^{q\circ,C} + [x_Bx_C/(x_B + x_C)] \times \{b_{BC}^{(0)} + b_{BC}^{(1)}[x_C/(x_B + x_C)] + \cdots\} \quad (9a)$$

for {A1 + A2 + ... + Aq + B + C} within $0 \leq (x_C/x_C^{q\circ}) \leq 1$ and by

$$x_\beta = \sum_i (x_i/x_i^{q\circ})x_\beta^{q\circ,i} + \sum_i \sum_k (x_ix_k/\sum_k x_k) \times \{b_{ik}^{(0)} + b_{ik}^{(1)}[x_k/(x_i + x_k)] + \cdots\} \quad (9b)$$

for {A1 + A2 + ... + Aq + B + C + ... + Z} within $0 \leq (x_i/x_i^{q\circ}) \leq 1$, where $b_{ik}^{(0)}$ and $b_{ik}^{(1)}$ are parameters. For example, the isopiestic behavior of PbO in the ternary slag {PbO (A) + SiO_2 (B) + B_2O_3 (C)} at 1273 K[28] may be given by $b_{BC}^{(0)} = -7.30a_A + 11.90a_A^2$ and $b_{BC}^{(1)} = b_{BC}^{(2)} = \cdots = 0$ within $0 \leq (x_C/x_C^{1\circ}) \leq 1$ and $0 \leq a_A \leq 1$. In one case of $b_{ik}^{(0)} = b_{ik}^{(1)} = \cdots = 0$ or $\sum_k x_k \rightarrow 0$, eq 9 yields the first general linear concentration rule at constant activities of A1, A2, ..., Aq[9] or the second extended ZSR rule of Wang:[1]

$$\tau_\beta = \sum_i (\tau_i/\tau_i^{q\circ})\tau_\beta^{q\circ,i} \quad (10a)$$

$$\sum_i (\tau_i/\tau_i^{q\circ}) = 1 \quad (10b)$$

$$\sum_i \{(m_i/m_\beta)/(m_i^{q\circ}/m_\beta^{q\circ,i})\} = 1 \quad (10c)$$

$$s_\beta = \sum_i (x_i/\sum_k x_k)s_\beta^{q\circ,i} \quad (10d)$$

within $0 \leq (\tau_i/\tau_i^{q\circ}) \leq 1$. For {A + B + C + ... + Z}, eq 10 reduces to the first general linear concentration rule at constant activities of A or the first extended ZSR rule of Wang:[1]

$$\tau_A = \sum_i (\tau_i/\tau_i^{1\circ})\tau_A^{1\circ,i} \quad (11a)$$

$$\sum_i (\tau_i/\tau_i^{1\circ}) = 1 \quad (11b)$$

$$s_A = \sum_i (x_i/\sum_k x_k)s_A^{1\circ,i} \quad (11c)$$

within $0 \leq (\tau_i/\tau_i^{1\circ}) \leq 1$. In another case of $[x_j/(x_B + x_j)] \rightarrow 0$, eq 9 yields eq 7, the second general linear concentration rule at constant activities of A1, A2, ..., Aq[9] or the second extended Turkdogan rule of Wang. For {A + B + C + ... + Z}, eq 7 reduces to eq 5, the second general linear concentration rule at constant activities of A or the first extended Turkdogan rule of Wang. For unsaturated aqueous solutions, eq 9 may be rewritten as[29]

$$(m_B/m_B^{1\circ}) + (m_C/m_C^{1\circ}) = 1 + [m_Bm_C/(m_B + m_C)] \times \{c_{BC}^{(0)} + c_{BC}^{(1)}[m_C/(m_B + m_C)] + c'_{BC}a_A\} \quad (12a)$$

for {water (A) + solute (B) + solute (C)} within $0 \leq (m_C/m_C^{1\circ}) \leq 1$ or as[30]

$$\sum_i (m_i/m_i^{1\circ}) = 1 + \sum_i \sum_k (m_im_k/\sum_k m_k) \times \{c_{ik}^{(0)} + c_{ik}^{(1)}[m_k/(m_i + m_k)] + c'_{ik}a_A\} \quad (12b)$$

for {water (A) + solute (B) + solute (C) + ... + solute (Z)} within $0 \leq (m_i/m_i^{1\circ}) \leq 1$, where $c_{ik}^{(0)}$, $c_{ik}^{(1)}$, and c'_{ik} are parameters; which are equivalent to eqs 4 and 6 in ref 31. For example, it was found that $c_{BC}^{(0)} = c_{BC}^{(1)} = c'_{BC} = 0$ at $a_A \geq 0.724$ and $c_{BC}^{(0)} = 0.2055$, $c_{BC}^{(1)} = 0$, and $c'_{BC} = -0.2839$ at $a_A < 0.724$ for {water (A) + HNO_3 (B) + $Th(NO_3)_4$ (C)}[32] at 25.0 °C, and $c_{BC}^{(0)} = c_{BC}^{(1)} = c'_{BC} = 0$ at about $a_A \geq 0.984$ and $c_{BC}^{(0)} \neq 0$ at about $a_A \leq 0.941$ for {water (A) + NaCl (B) + NaPAA (C)}[33] at 25.0 °C. Therefore, in the case that the solution {B + C + ... + Z} deviates from the Raoult law and the classically ideal solution model and obeys the Henry law and the classically dilute solution model, the two extended ZSR rules of Wang, eqs 10 and 11, and the partial ideal solution model and ideal-like solution model may be valid for $\{A + B + C + ... + Z\}$ and $\{A1 + A2 + ... + Aq + B + C + ... + Z\}$, respectively, in the B, C, ..., Z poor ranges, while the two extended Turkdogan rules of Wang, eqs 5 and 7, and the partial dilute solution model and dilute-like solution model may hold in the A1, A2, ..., A*q* poor ranges.

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