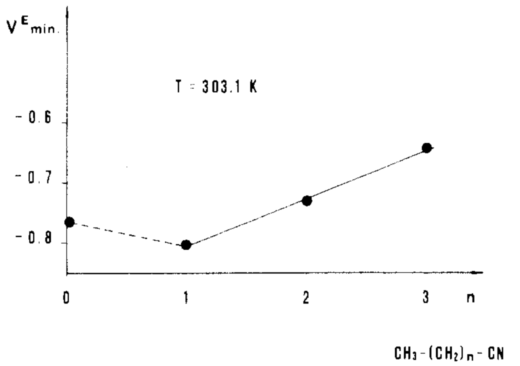

Figure 3. Values of the minimum, $V^E_{min}/(cm^3\ mol^{-1})$, in excess-volume curves, at 303.1 K, plotted against n (number of CH_2 groups in $CH_3-(CH_2)_n-CN$).

basis a predominance of self-association of nitriles with increasing temperature on interactions with sulfolane appears as an available interpretation of the increased volume contractions.

The plot in Figure 3 shows that the depth of the minimum in excess volumes (plot refers to measured excess volumes at 303.1 K) exhibits a linear decrease with an increase in the number of CH_2 groups in the nitrile molecule. This behavior may indicate that the main factor in determining the importance of interactions of all kinds rests in steric hindrance since the polarity of the molecule is unaffected by chain length (μ = 3.57 D). Deviating from the straight line, however, is the point for the acetonitrile–sulfolane system (*8*).

The lack of CH_2 groups in acetonitrile results indeed in a lowered polarity of the molecule because of the transmission to the $-{}^+C{=}N{:}^-$ group of the inductive effect of $-CH_3$ (the acetonitrile electric moment is in fact 3.44 D) and in an inordinate change in the steric hindrance. Because of these two effects, the energies of interactions of all kinds would be modified and the partition equilibrium of the nitrile between self-association and interaction with sulfolane altered.

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Method To Assess the Equilibrium MO_x–"MC_y"–C–CO. The System ZrO_2–"ZrC"–C–CO

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A method to assess the equilibria in the systems MO_x–"MC_y"–C–CO of transition or actinide metals has been proposed. As an example, the equilibrium ZrO_2–"ZrC"–C–CO has been assessed. The equilibrium CO pressure expressed as $\log P_{CO,torr} = 11.51 - 16580/T$ is suggested. Third-law treatment of the P_{CO} gives $\Delta H_f{}^\circ_{298}$ ($ZrC_{1.00}$) = −49.5 kcal/mol, which agrees with that of combustion calorimetry.

A transition or actinide metal carbide which is in equilibrium with the metal oxides, C, and CO at high temperatures usually contains oxygen and is supposedly nonstoichiometric. The oxycarbides, i.e., the carbide dissolving oxygen, of group 4 and actinide elements are so stable that it is hard to obtain the oxygen-free carbides. This is a cause of discrepancies among published thermodynamic data of those carbides. The data obtained from the equilibrium MO_x–"MC_y"–C–CO have been cited with reserve: the oxygen will influence the stability of the carbide to an unknown extent. Besides, the CO pressure measurement is certainly difficult task, and agreement between authors is seldom found.

Theoretically one can calculate the equilibrium CO pressure (P_{CO}) over MO_x–"MC_y"–C–CO by the relations

$$(x/2)\,RT \ln P_{O_2} + RT \ln a_M = \Delta G^\circ_{MO_x} \tag{1}$$

where $a(MO_x) = 1$

$$RT \ln P_{CO} + \Delta G^\circ_{CO} = \tfrac{1}{2} RT \ln P_{O_2} \tag{2}$$

and, therefore

$$RT \ln P_{CO} = -\Delta G^\circ_{CO} + (1/x)(\Delta G^\circ_{MO_x} - RT \ln a_M) \tag{3}$$

where ΔG° is the molar free energy of formation and a_M the activity of the metal in "MC_y" in equilibrium with MO_x and C. If the metal activity a_M in "MC_y" is approximately equal to a°_M in the pure carbon-saturated MC_y, eq 3 reduces to

$$RT \ln P_{CO} = -\Delta G^\circ_{CO} + (1/x)(\Delta G^\circ_{MO_x} - \Delta G^\circ_{MC_y}) \tag{4}$$

where $\Delta G^\circ_{MC_y}$ is the molar free energy of formation of the pure carbide. This is simply the equation for the hypothetical reaction

$$MO_x + (x + y)C = MC_y + xCO \tag{5}$$

We shall seek the condition for $a_M = a^\circ_M$. Assuming the carbon activity $a_C = 1$ in the phase regions "MC_y" + C and MO_x + "MC_y" + C and "MC_y" = $MC_{y-\alpha}O_\beta$ in the latter region, the Gibbs–Duhem relation gives

$$\Delta G^\circ_{MC_{y-\alpha}O_\beta} = \Delta G^\circ_{MC_y} + \tfrac{1}{2}\int_0^\beta \Delta \bar{G}_{O_2}\, dz \tag{6}$$

Table I. Third-Law Calculation of $\Delta H_f{}^\circ{}_{298}(\mathrm{ZrC}_{1.00})$

	$-\Delta\mathrm{fef}_T$,[a]	$\Delta H^\circ{}_{298}$,[b] kcal/mol				$-\Delta H_f{}^\circ{}_{298}(\mathrm{ZrC})$,[c] kcal/mol			
T, K	cal/(mol K)	Prescott	Ouensanga	Storms[d]	eq 17	Prescott	Ouensanga	Storms	eq 17
1700	84.27	161.36	160.97	160.43	160.73	48.9	49.3	49.8	49.5
1800	84.00	161.44	160.75	160.58	160.78	48.8	49.5	49.7	49.5
1900	83.75	161.51	160.51	160.72	160.82	48.7	49.8	49.5	49.4
2000	83.51	161.55	160.25	160.83	160.82	48.7	50.0	49.4	49.4

[a] $\Delta\mathrm{fef}_T = \mathrm{fef}_T(\mathrm{ZrC}) + 2\mathrm{fef}_T(\mathrm{CO}) - \mathrm{fef}_T(\mathrm{ZrO_2}) - 3\mathrm{fef}_T(\mathrm{C})$. [b] $\Delta H^\circ{}_{298} = T(-2R \ln P_{\mathrm{Co}} - \Delta\mathrm{fef}_T)$. [c] $\Delta H_f{}^\circ{}_{298}(\mathrm{ZrO_2}) = -263.1 \pm 0.5$ kcal/mol, $\Delta H_f{}^\circ{}_{298}(\mathrm{CO}) = -26.42 \pm 0.01$ kcal/mol. [d] By eq 12 calculated from a_{Zr} in $\mathrm{ZrC}_{1.00}$.

where $\Delta\bar{G}_{\mathrm{O_2}}$ is the partial molar energy of O_2 and z the atomic fraction $N_{\mathrm{O}}/N_{\mathrm{M}}$ in the region "MC_y" + C. Equation 6 can be written

$$\Delta G^\circ{}_{\mathrm{MC}_{y-\alpha}\mathrm{O}_\beta} = \Delta G^\circ{}_{\mathrm{MC}_y} + \beta\Delta G^\circ{}_{\mathrm{CO}} + RT\int_0^\beta \ln P_{\mathrm{CO}}{}^* \, dz$$

$$= RT \ln a^\circ{}_{\mathrm{M}} + \beta\Delta G^\circ{}_{\mathrm{CO}} + RT\int_0^\beta \ln P_{\mathrm{CO}}{}^* \, dz \qquad (7)$$

where $P_{\mathrm{CO}}{}^*$ is the CO pressure over the region "MC_y" + C. On the other hand, $\Delta G^\circ{}_{\mathrm{MC}_{y-\alpha}\mathrm{O}_\beta}$ can be written

$$\Delta G^\circ{}_{\mathrm{MC}_{y-\alpha}\mathrm{O}_\beta} = RT \ln a_{\mathrm{M}} + \tfrac{1}{2}RT \ln P_{\mathrm{O_2}}$$

$$= RT \ln a_{\mathrm{M}} + \beta\Delta G^\circ{}_{\mathrm{CO}} + \beta\, RT \ln P_{\mathrm{CO}} \qquad (8)$$

Therefore the condition for $a_{\mathrm{M}} = a^\circ{}_{\mathrm{M}}$ is

$$RT\int_0^\beta \ln P_{\mathrm{CO}}{}^* \, dz \doteq \beta RT \ln P_{\mathrm{CO}} \qquad (9)$$

The most simple case, but probably an unrealistic one, is that in which $P_{\mathrm{CO}}{}^*$ is constant throughout the phase region "MC_y" + C. The other case is that in which β is small enough to make both sides of eq 9 trivial.

If $a_{\mathrm{M}} \doteq a^\circ{}_{\mathrm{M}}$, the following arguments hold: (1) One can calculate the P_{CO} by eq 3 or 4 knowing neither thermodynamic properties nor exact composition of "MC_y" in equilibrium with MO_x, C, and CO. (2) Conversely, one can estimate the thermodynamic properties of the pure carbon-saturated carbide from the equilibrium MO_x–"MC_y"–C–CO. (3) However, without further information such as oxygen content in "MC_y", one cannot estimate the effect of oxygen dissolution on the stability of the carbide.

These points will be illustrated by the following discussion on the equilibrium $\mathrm{ZrO_2}$–"ZrC"–C–CO. For the calculations, thermodynamic data were taken as follows: those for C and CO from the JANAF tables (*1*); thermal functions and molar free energies of Zr and $\mathrm{ZrO_2}$ calculated by me from the data suggested by Alcock et al. (*2*); thermal function of ZrC calculated by Storms and Griffin for $\mathrm{ZrC}_{0.96}$ (*3*).

The hypothetical reaction in the present case is

$$\mathrm{ZrO_2} + 3\mathrm{C} = \mathrm{ZrC} + 2\mathrm{CO} \qquad (10)$$

The $\mathrm{ZrO_2}$ in this system may be slightly hypostoichiometric. Ouensanga and Dode (*4*) have assigned the composition $\mathrm{ZrO}_{1.99\pm0.01}$ at 1800 K. Since such small deviation from stoichiometry is considered insignificant compared with overall uncertainties of the relevant thermodynamic data, it is neglected in the following discussion.

Storms and Griffin (*3*) have measured a_{Zr} in $\mathrm{ZrC}_{1.00}$

$$\ln a_{\mathrm{Zr}} = 2.160 - 26625/T \qquad (11)$$

Combining eq 3 with eq 11, one obtains

$$\log P_{\mathrm{CO,torr}} = 11.39 - 16350/T \quad (1700\text{–}2000\ \mathrm{K}) \qquad (12)$$

Equation 12 will be compared with those measured on the system $\mathrm{ZrO_2}$–"ZrC"–C–CO by several investigators.

$$\log P_{\mathrm{CO,torr}} = 11.80 - 17100/T \quad (\text{ref } 4) \qquad (13)$$

$$\log P_{\mathrm{CO,torr}} = 11.47 - 16580/T \quad (\text{ref } 5) \qquad (14)$$

$$\log P_{\mathrm{CO,torr}} = 10.75 - 15700/T \quad (\text{ref } 6) \qquad (15)$$

$$\log P_{\mathrm{CO,torr}} = 9.43 - 16100/T \quad (\text{ref } 7) \qquad (16)$$

The P_{CO} by Hollahan and Gregory and that by Kutsev et al. are too low compared with that in eq 12. In order to assess the rest of the measurements (eq 13 and 14) together with eq 12, the third-law heat of formation of $\mathrm{ZrC}_{1.00}$ was calculated in Table I. Those values of $\Delta H_f{}^\circ{}_{298}$ will be compared with $\Delta H_f{}^\circ{}_{298}(\mathrm{ZrC}_{1.00}) = -49.5 \pm 0.6$ kcal/mol by combustion calorimetry by Baker et al. (*8*). In determining $\Delta H_f{}^\circ{}_{298}$, Baker et al. have corrected for the unavoidable oxygen impurity by a proper method. By comparison, the P_{CO} at abut 1800 K by Ouensanga and Dode and that calculated from a_{Zr} are satisfactory, but the temperature dependence of the former seems a little too large and that of the latter a little too small; the P_{CO} by Prescott and Hincke is a little lower, but its temperature dependence fits better to that of $\Delta\mathrm{fef}_T$. As a compromise, I tentatively suggest

$$\log P_{\mathrm{CO,torr}} = 11.51 - 16580/T \quad (1700\text{–}2000\ \mathrm{K}) \qquad (17)$$

The third-law heat of formation of this P_{CO} gives an average $\Delta H_f{}^\circ{}_{298} = -49.5$ kcal/mol, though the error limit will amount to ±4 kcal/mol due to the cumulative uncertainties from the relevant thermodynamic data.

Though the third-law heats of formation agree well with that obtained from combustion of the carbide, it does not mean that the stability of "ZrC" is only negligibly affected by oxygen dissolution. Ouensanga and Dode (*4*) determined the composition of "ZrC" to be $\mathrm{ZrC}_{0.835}\mathrm{O}_{0.06}$ at about 1800 K. Therefore, the real reaction may be

$$\mathrm{ZrO}_{1.99} + 2.765\mathrm{C} = \mathrm{ZrC}_{0.835}\mathrm{O}_{0.06} + 1.93\mathrm{CO} \qquad (18)$$

instead of the hypothetical eq 12. In order to give the same P_{CO} as eq 17, "ZrC" should be stabilized by

$$(2 - 1.93)(\Delta G^\circ{}_{\mathrm{CO}} + RT \ln P_{\mathrm{CO}}) = -5\ \mathrm{kcal/mol} \quad \text{at } 1800\ \mathrm{K} \qquad (19)$$

As noted from this equation, a small error in O/Zr of "ZrC" will significantly affect the estimation.

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Solubility of Cuprous Chloride in Various Soluble Aqueous Chlorides

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Smoothed tables of the solubility of CuCl in aqueous HCl and aqueous NaCl from 0.01 to 6.0 M and from 0 to 100 °C are presented. Similar tables are given, for 25 °C only, for mixtures of HCl and NaCl, and for solutions in aqueous KCl, NH_4Cl, $CuCl_2$, and $FeCl_2$. The procedures and parameters necessary for calculation of the solubility at other concentrations and temperatures are given. Simple methods for handling solubility in complex mixtures and in cases where experimental information is scant are discussed.

Introduction

The substantial solubility of cuprous chloride (Cu^ICl) in various aqueous chlorides arises almost entirely from the formation of chloro complexes such as $CuCl_2^-$, $CuCl_3^{2-}$, etc. Calculation of its solubility requires knowledge of the equilibrium constants for formation of the important complexes and a set of virial parameters adequate to represent the activity coefficients of the ions present in the solutions. In previous work (*1*, *2*) I have evaluated the equilibrium constants at 25 °C for the formation of $CuCl_2^-$, $CuCl_3^{2-}$, $Cu_2Cl_4^{2-}$, and triply charged complexes (represented as $Cu_3Cl_6^{3-}$), from CuCl(s), the corresponding heats of formation, and sets of virial parameters suitable for calculation of the activity coefficients of the complex species in a number of aqueous chlorides. The principal purpose of this paper is to present tables of solubility of CuCl as a function of concentration and temperature (0–100 °C) in various aqueous media and the parameters necessary for calculation of the solubility under other conditions. In addition methods are discussed for approximate correlations of solubilities in cases where data are not sufficient for detailed analysis.

Procedure for Calculation of Solubilities

Table I. Equilibrium Constants and Heats of Reaction[a]

complex formed	K_{298}	ΔH, cal/mol
$CuCl_2^-$	0.0604	6669
$CuCl_3^{2-}$	0.0128	3450
$Cu_2Cl_4^{2-}$	8.24×10^{-4}	6700
$Cu_3Cl_6^{3-}$	3.41×10^{-5}	0.0
combined^{2-}	0.0144	4010

[a] Note that the values given for the higher complexes are somewhat different from those in ref *2*. The values for $Cu_2Cl_4^{2-}$ and $Cu_3Cl_6^{3-}$ are hard to separate; the values above give somewhat better representation of the limited data available at 0 and 100 °C.

Table II. Equations Used for Calculation of Activity Coefficients[a]

$$\ln \gamma_N = (z_N)^2 f^\gamma + 2\sum_a M_a[B_{Na} + (\Sigma Mz)C_{Na}] + \sum_c\sum_a M_cM_a[(z_N)^2B'_{ca} + z_NC_{ca}]$$

$$\ln \gamma_X = (z_X)^2 f^\gamma + 2\sum_c M_c[B_{cX} + (\Sigma Mz)C_{cX}] + \sum_c\sum_a M_cM_a[(z_X)^2B'_{ca} - z_XC_{ca}]$$

with

$$f^\gamma = -A_\phi\left[\frac{I^{1/2}}{1 + 1.2I^{1/2}} + \frac{2}{1.2}\ln(1 + 1.2I^{1/2})\right]$$

$$B_{NX} = \beta^{(0)}{}_{NX} + (2\beta^{(1)}{}_{NX}/\alpha^2I)\{1 - [1 + \alpha I^{1/2}] \times \exp(-\alpha I^{1/2})\}$$

$$B'_{NX} = (2\beta^{(1)}{}_{NX}/\alpha^2I^2)\{-1 + [1 + \alpha I^{1/2} + (1/2)\alpha^2 I]\exp(-\alpha I^{1/2})\}$$

$$(\Sigma Mz) = \sum_c M_cz_c$$

$$\alpha = 2.0$$

[a] (1) For 2–2 and higher valence type electrolytes an additional parameter $\beta^{(2)}$ must be added. (2) For mixtures, terms of the form $\Sigma_i\Sigma_jM_iM_j\psi_{Nij}$ should be added to the expressions for ln γ to account for interactions between three different ions. These terms have been omitted for simplicity in the present treatment. (3) M represents mol/L throughout. (See ref *4* for details on both of the above matters.)

The formation of a given complex species is represented by an equation such as

$$m\mathrm{CuCl(s)} + n\mathrm{Cl}^- = (\mathrm{Cu}_m\mathrm{Cl}_{m+n})^{n-} \tag{1}$$

The equilibrium constant for the *i*th complex is then

$$K_i = \frac{a_i}{(a_{\mathrm{Cl}^-})^{n_i}} = \frac{c_i}{(c_{\mathrm{Cl}^-})^{n_i}}\frac{\gamma_i}{(\gamma_{\mathrm{Cl}^-})^{n_i}} \tag{2}$$

so that the concentration (c_i) of the complex can be calculated from that of Cl^-, provided that the necessary K_i and the activity coefficients are known. Table I gives values of the equilibrium constants at 25 °C and the corresponding heats of reaction for the complex species considered hereafter (*1*, *2*). Activity coefficients can be calculated by using the virial model developed by Pitzer and co-workers (*3*, *4*), in which the second virial coefficient *B* for a given ion pair depends on both ionic strength and ionic concentrations, while the third virial coefficient *C* is independent of both. The necessary equations are represented by eq 12–15 of Pitzer and Kim (*4*), with three modifications. First, molarity (*M*, mol/L) has been used in place of molality (*m*, mol/(1000 g of solvent)) throughout. (See discussion in ref *1*.) Second, only the principal terms in the equations have been found necessary to represent the solubility data. Finally, the

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