

where  $X = x_a/x_0$ ,  $x_a$  = solubility (mole fraction) of ammonium alum (24 H<sub>2</sub>O) in the ternary (aqueous alcohol) solution,  $x_0$  = solubility (mole fraction) of ammonium alum (24 H<sub>2</sub>O) in the binary (aqueous) solution,  $m$  = molality of alcohol in aqueous solution (mol of alcohol/kg of water), and  $K_1$ ,  $K_2$ ,  $C$  = constants. An example of one of the quadratic regression fits is shown in Figure 2 for alum-water-methanol at 20 °C. In all cases, the constant  $C$  in eq 1 was found to be insignificant, and it is thus possible to estimate the solubilities (mole fraction  $x_a$ ) of alum in the aqueous alcohol systems, with an average precision of  $\pm 2.5\%$  from the simpler relationship

$$\log X = K_1 m + K_2 m^2 \quad (2)$$

Values of  $K_1$  and  $K_2$  are listed in Tables I-III.

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# Thermodynamic Properties of Binary Mixtures Involving Sulfolane.

## 1. Excess Volumes on Mixing Sulfolane and Propionitrile, Butyronitrile, and Valeronitrile

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**Excess volumes on mixing sulfolane and propionitrile, butyronitrile, and valeronitrile were measured over the entire composition range  $0 \leq x \leq 1$ , at four temperatures between 293.1 and 323.1 K. All mixtures exhibit negative excess volumes with a minimum which occurs approximately at  $x = 0.5$  in the case of the butyronitrile-sulfolane and valeronitrile-sulfolane systems; it is shifted toward the propionitrile-rich region in the case of the propionitrile-sulfolane system. The magnitude of the minimum steadily increases with temperature and decreasing nitrile chain length. Data are interpreted in terms of moderate interactions of all kinds decreasing in importance with increasing nitrile carbon chain length and an increase of the nitrile self-association with respect to the interactions with sulfolane as the temperature increases.**

### Introduction

Our previous measurements (1-9) of excess properties of liquid mixtures involving sulfolane and a large number of selected apolar and polar substances (water, normal and branched alcohols, benzene, nitrobenzene, carbon tetrachloride, dioxane, nitriles) are indicative of only weak interactions between unlike molecules. Furthermore, our recent investigations (10) on the nitrobenzene-sulfolane solid-liquid phase diagram strongly support the supposition of an ideal behavior; excess enthalpies on mixing benzene and sulfolane have been found by Carvo (11) to be so small that this system can be treated as athermal, and this is in good agreement with our previous interpretation of viscosity, density, dielectric-constant data and solid-liquid equilibrium temperatures (3).

In other words, sulfolane, in these binary systems, is suspected to behave as an almost inert diluent, in spite of its fairly high polarity ( $\mu = 4.8$  D), presumably because of the steric hindrance of its globular molecules.

These statements prompted us to collect further data on sulfolane solutions for a more complete review. We present

herewith excess volumes on mixing of some binary systems involving sulfolane and propionitrile, butyronitrile, and valeronitrile. Data on the acetonitrile-sulfolane system have been published previously (8).

Our choice of nitrile series has been guided by a regular varying molecular size of selected nitriles without inordinate alteration in molecular structure and the effective polarity of the nitrile ( $\mu = 3.57$  D). Hence, moderate interactions, if any, between like and unlike molecules, mainly dipole-dipole interactions, are expected to occur in these systems, dominated by steric factors univocally.

### Experimental Section

**Materials.** Sulfolane kindly supplied by Shell Italia was purified and dried carefully, as already reported (12); the melting point of the final product was 301.61 K, in close agreement with our own previous data and the most reliable literature data (13); BDH nitriles (propionitrile, butyronitrile, and valeronitrile) were dried and distilled from anhydrous P<sub>2</sub>O<sub>5</sub> by using a 1-m, glass-packed fractionating column as recommended in the literature (14). Immediately before use, all materials were degassed by repeated freeze-thaw cycles. Solutions were made by weight (reduced to mass) and then stored in dark containers and protected from moisture as far as possible.

The apparatus (an Anton Paar DMA 60 digital densimeter) and the procedure in measuring densities were described elsewhere (8). The maximum error in the densities was estimated to be  $3 \times 10^{-5}$  g cm<sup>-3</sup>.

Densities of solutions were measured over the entire composition range, at different temperatures. Working temperatures were 293.12, 303.07, 313.10, and 323.10 K in the case of the propionitrile-sulfolane and butyronitrile-sulfolane systems (data at 323.10 K were not taken in the case of butyronitrile). The temperatures were 303.16, 313.16, 323.16, and 333.16 K in the case of the valeronitrile-sulfolane system.

For the sake of uniformity with previous work, the sulfolane was identified as component (2) and the other substance as component (1); compositions were stated as mole fractions,  $x_2$ .

Table I. Molar Volumes,  $V^{\circ}$ , Parameters,  $A, B, C$ , and  $D$ , and Standard Deviations,  $\sigma$ , of the Smoothing Equations

$T/K$	$V_1^{\circ}/(\text{cm}^3 \text{ mol}^{-1})$	$V_2^{\circ}/(\text{cm}^3 \text{ mol}^{-1})$	$A$	$B$	$C$	$D$	$\sigma/(\text{cm}^3 \text{ mol}^{-1})$
Propionitrile (1)-Sulfolane (2)							
293.12	70.465	(94.496)	-2.907	0.762	-0.094	0.222	0.004
303.07	71.379	95.182	-3.159	0.731	-0.304	0.098	0.005
313.10	72.343	95.863	-3.461	0.909	-0.341	0.037	0.003
323.10	73.324	96.549	-3.843	0.974	-0.691	0.024	0.005
Butyronitrile (1)-Sulfolane (2)							
293.12	87.371	(94.496)	-2.674	0.550	0.189		0.010
303.07	88.409	95.178	-2.904	0.443	0.092		0.005
313.10	89.501	95.862	-3.210	0.499	-0.090		0.006
Valeronitrile (1)-Sulfolane (2)							
293.16	104.036	(94.499)	-2.416	0.427	0.352		0.009
303.16	105.190	95.199	-2.571	0.247	-0.064		0.007
313.16	106.365	95.868	-2.805	0.169	-0.110		0.003
323.16	107.568	96.552	-2.997	0.172	-0.089		0.003

Table II. Molar Excess Volumes,  $V^E$ , of Propionitrile (1)-Sulfolane (2) Mixtures, at Four Temperatures, and Deviations  $\delta V^E$  from the Smoothing Equations

$x_2$	293.12 K		303.07 K		313.10 K		323.10 K	
	$V^E/(\text{cm}^3 \text{ mol}^{-1})$	$10^3 \delta V^E/(\text{cm}^3 \text{ mol}^{-1})$	$V^E/(\text{cm}^3 \text{ mol}^{-1})$	$10^3 \delta V^E/(\text{cm}^3 \text{ mol}^{-1})$	$V^E/(\text{cm}^3 \text{ mol}^{-1})$	$10^3 \delta V^E/(\text{cm}^3 \text{ mol}^{-1})$	$V^E/(\text{cm}^3 \text{ mol}^{-1})$	$10^3 \delta V^E/(\text{cm}^3 \text{ mol}^{-1})$
0.0808	-0.279	-1	-0.305	-5	-0.335	-2	-0.391	-8
0.1470	-0.447	1	-0.488	-4	-0.535	2	-0.610	2
0.2169	-0.578	1	-0.631	-5	-0.695	0	-0.781	4
0.3223	-0.698	1	-0.761	-5	-0.838	-2	-0.933	1
0.4237	-0.746	-7	-0.803	-3	-0.882	-1	-0.980	-1
0.5044	-0.719	6	-0.787	1	-0.858	5	-0.962	-3
0.6268	-0.634	1	-0.697	3	-0.766	-5	-0.854	-2
0.7411	-0.489	-2	-0.545	5	-0.592	2	-0.671	7
0.8628	-0.277	-3	-0.320	6	-0.349	2	-0.412	1
0.9293	-0.139	4	-0.175	2	-0.194	-3	-0.237	-7

Table III. Molar Excess Volumes,  $V^E$ , of Butyronitrile (1)-Sulfolane (2) Mixtures, at Three Temperatures, and Deviations  $\delta V^E$  from the Smoothing Equations

$x_2$	293.12 K		303.07 K		313.10 K	
	$V^E/(\text{cm}^3 \text{ mol}^{-1})$	$10^3 \delta V^E/(\text{cm}^3 \text{ mol}^{-1})$	$V^E/(\text{cm}^3 \text{ mol}^{-1})$	$10^3 \delta V^E/(\text{cm}^3 \text{ mol}^{-1})$	$V^E/(\text{cm}^3 \text{ mol}^{-1})$	$10^3 \delta V^E/(\text{cm}^3 \text{ mol}^{-1})$
0.0433	-0.125	0	-0.133	1	-0.146	9
0.0859	-0.234	2	-0.253	-1	-0.297	-8
0.1506	-0.379	0	-0.413	-8	-0.468	-7
0.2587	-0.547	8	-0.595	-1	-0.663	3
0.3499	-0.633	9	-0.690	-1	-0.766	0
0.4774	-0.659	12	-0.720	10	-0.798	8
0.5509	-0.639	8	-0.700	7	-0.774	8
0.6740	-0.552	-12	-0.604	-2	-0.668	1
0.7723	-0.424	-14	-0.470	-7	-0.522	-1
0.8885	-0.219	-8	-0.253	-5	-0.290	-5
0.9414	-0.107	6	-0.133	2	-0.161	-4

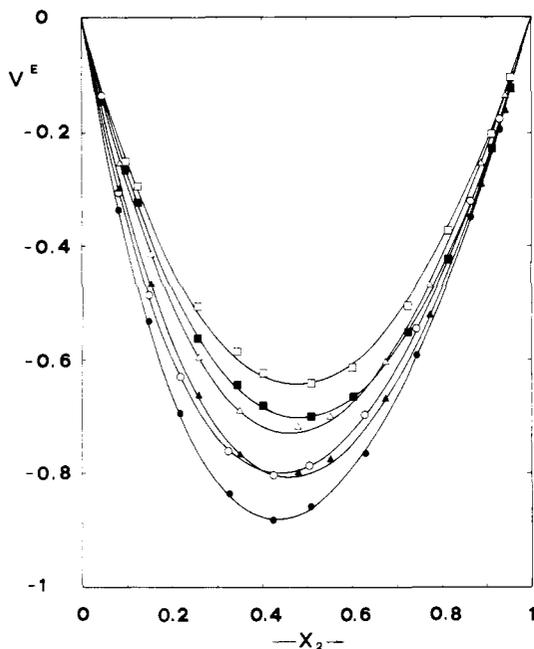
Table IV. Molar Excess Volumes,  $V^E$ , of Valeronitrile (1)-Sulfolane (2) Mixtures, at Four Temperatures, and Deviations  $\delta V^E$  from the Smoothing Equations

$x_2$	293.16 K		303.16 K		313.16 K		323.16 K	
	$V^E/(\text{cm}^3 \text{ mol}^{-1})$	$10^3 \delta V^E/(\text{cm}^3 \text{ mol}^{-1})$	$V^E/(\text{cm}^3 \text{ mol}^{-1})$	$10^3 \delta V^E/(\text{cm}^3 \text{ mol}^{-1})$	$V^E/(\text{cm}^3 \text{ mol}^{-1})$	$10^3 \delta V^E/(\text{cm}^3 \text{ mol}^{-1})$	$V^E/(\text{cm}^3 \text{ mol}^{-1})$	$10^3 \delta V^E/(\text{cm}^3 \text{ mol}^{-1})$
0.0966	-0.226	-5	-0.250	-5	-0.263	0	-0.277	2
0.1233	-0.275	-1	-0.295	7	-0.322	2	-0.346	-3
0.2549	-0.468	15	-0.508	6	-0.560	-6	-0.592	-3
0.3397	-0.561	4	-0.587	9	-0.644	0	-0.689	-2
0.4037	-0.596	2	-0.625	6	-0.681	3	-0.728	2
0.5087	-0.590	12	-0.641	0	-0.697	3	-0.745	3
0.6022	-0.564	-10	-0.616	-12	-0.666	-1	-0.716	-6
0.7207	-0.440	-5	-0.506	-8	-0.550	4	-0.590	1
0.8119	-0.314	-7	-0.373	0	-0.423	-4	-0.447	0
0.9109	-0.161	-13	-0.201	-5	-0.223	-1	-0.238	-1
0.9535	-0.069	8	-0.105	1	-0.121	1	-0.129	0

## Results

The molar volumes for pure components (Table I) are in close agreement ( $0.005 \text{ cm}^3$ ) with the most reliable literature

data (13, 14). The values for pure sulfolane, at temperatures lower than 301.61 K, appear in parenthesis because these are extrapolated values. All measurements refer to  $p = 1 \text{ atm}$ . The accuracy in measuring temperatures was  $\pm 0.005 \text{ }^\circ\text{C}$ .



**Figure 1.** Excess volumes  $V^E/(\text{cm}^3 \text{mol}^{-1})$  plotted against sulfolane mole fraction,  $x_2$ , at 301.1 K (open symbols) and 313.1 K (full symbols) for the following three systems: propionitrile (1)-sulfolane (2); circles, butyronitrile (1)-sulfolane (2); triangles, valeronitrile (1)-sulfolane (2) squares.

**Volumes of Mixing.** Measured excess volumes on mixing nitrile and sulfolane are summarized in Tables II-IV. Only data at 301.1 and 313.1 K are shown graphically in Figure 1 as a function of composition for each binary system, and this is in order to differentiate the behavior of each nitrile with respect to the others, avoiding at the same time incidental superposition of plots.

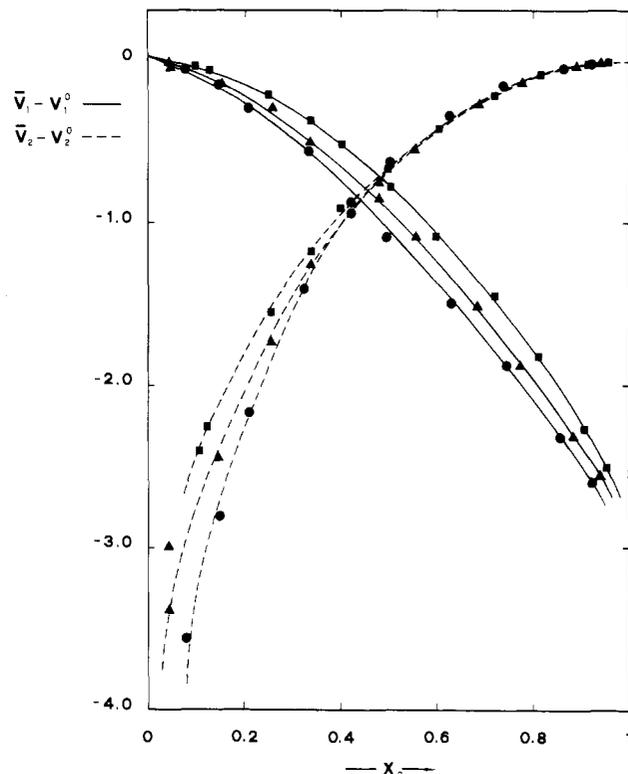
All mixtures exhibit negative excess volumes over the entire composition range with a sharp minimum, in no case exceeding  $-1 \text{ cm}^3 \text{mol}^{-1}$ ; it occurs approximately at  $0.5x_2$  in the case of the butyronitrile (1)-sulfolane (2) and valeronitrile (1)-sulfolane (2) systems, whereas it is shifted toward the nitrile-rich region in the case of the propionitrile (1)-sulfolane (2) system; the magnitude of the minimum increases steadily with temperature and with decreasing molar size of the nitrile.

The experimental results for the three binary systems were fitted by a least-squares computer program to the expression

$$V^E/(\text{cm}^3 \text{mol}^{-1}) = x_1 x_2 \{ A + B(x_2 - x_1) + C(x_2 - x_1)^2 + D(x_2 - x_1)^3 \dots \} \quad (1)$$

The parameters ( $A$ ,  $B$ ,  $C$ ,  $D$ ) for each system are listed in Table I. These are based on the lowest values of  $\{(\sum \delta V^E)^2 / (s - m)\}^{1/2} = \sigma$ , in which  $\delta V^E = V^E_{\text{expt}} - V^E_{\text{calcd}}$ ,  $s$  is the number of experimental points, and  $m$  is the number of parameters.

$V^E$  and  $\delta V^E$  values, at all of the working temperatures and over the entire composition range, are given in Table II (propionitrile (1)-sulfolane (2) system), Table III (butyronitrile (1)-sulfolane (2) system), and Table IV (valeronitrile (1)-sulfolane (2) system). In the case of the first system, a four-parameter equation was needed to obtain the fit of the experimental results; three-parameter equations were sufficient in the case of the last two systems. This was as expected, according to the higher symmetry of excess volume-composition curves. Relative partial molar volumes,  $\bar{V} - V^\circ$ , for both of the components of the three binary systems, derived from eq 1, at 313.1 K, are plotted in Figure 2 as a function of sulfolane mole fraction,  $x_2$ . Only slight deviations from volumes of pure substances are observed for both of the components of the three systems. These are more noticeable however in the case of nitriles than



**Figure 2.** Relative molar partial volumes,  $\bar{V} - V^\circ/(\text{cm}^3 \text{mol}^{-1})$ , of components plotted against sulfolane mole fraction,  $x_2$ , at 313.1 K, for the three systems: (●) propionitrile (1)-sulfolane (2); (▲) butyronitrile (1)-sulfolane (2); (■) valeronitrile (1)-sulfolane (2).

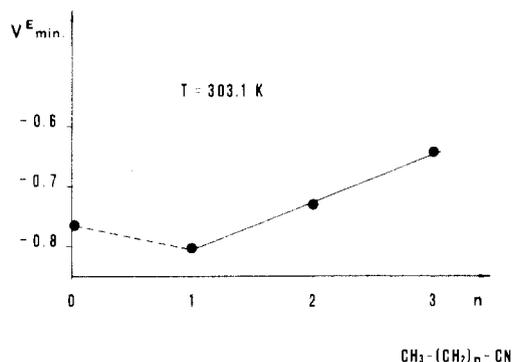
sulfolane and but slightly influenced by temperature.

## Discussion

The magnitude of the measured excess functions in the three systems is indicative of only moderate interactions of all kinds which decrease steadily with increasing molar size of the nitriles. The shapes of the excess volume vs. composition curves may be ascribed mainly to the difference in molar volumes of the two components. The curves indeed, as previously pointed out, are almost symmetrical in the case of the valeronitrile (1)-sulfolane (2) and butyronitrile (1)-sulfolane (2) systems (the molar volume of sulfolane being about  $8 \text{ cm}^3$  larger than the butyronitrile molar volume and about  $9 \text{ cm}^3$  smaller than the valeronitrile molar volume).

In the case of propionitrile, the difference in molar volumes of the two components amounts to  $\sim 24 \text{ cm}^3$ ; such an effect results in a characteristic skewing of the minimum in the direction of the smaller component (see Figure 1).

The minimum depends on the superposition of the effects arising from steric factors, interactions between unlike molecules, and nitrile self-association. The self-association is stronger when the unlike association is weakened. Both of these effects presumably arise from dipole-dipole interactions, which decrease with chain length, and should result in volume contractions. The supposition of a predominance of the association product with a more compact structure with increasing temperature is supported by the observed deepening of the minimum with temperature. It is reasonable to expect a more compact structure for the nitrile self-association product rather than the sulfolane-nitrile complex. Owing to the steric hindrance of the sulfolane globular molecule, only the exposed negative end of the dipole may be involved in complex formation. This implies that nitrile molecules must have proper orientation for interaction, and therefore an expanded structure and weak interactions result, which easily are disturbed by thermal motions and a lengthening of carbon chain. On this



**Figure 3.** Values of the minimum,  $V_{\min}^E$  (cm<sup>3</sup> mol<sup>-1</sup>), in excess-volume curves, at 303.1 K, plotted against  $n$  (number of CH<sub>2</sub> groups in CH<sub>3</sub>-(CH<sub>2</sub>)<sub>n</sub>-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<sub>2</sub> 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 ( $\mu = 3.57$  D). Deviating from the straight line, however, is the point for the acetonitrile-sulfolane system ( $\delta$ ).

The lack of CH<sub>2</sub> groups in acetonitrile results indeed in a lowered polarity of the molecule because of the transmission to the  $\text{---}^+\text{C}=\text{N:}^-$  group of the inductive effect of  $\text{---CH}_3$  (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 $\text{MO}_x$ - $\text{MC}_y$ -C-CO. The System $\text{ZrO}_2$ - $\text{ZrC}$ -C-CO

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**A method to assess the equilibria in the systems  $\text{MO}_x$ - $\text{MC}_y$ -C-CO of transition or actinide metals has been proposed. As an example, the equilibrium  $\text{ZrO}_2$ - $\text{ZrC}$ -C-CO has been assessed. The equilibrium CO pressure expressed as  $\log P_{\text{CO,100r}} = 11.51 - 16580/T$  is suggested. Third-law treatment of the  $P_{\text{CO}}$  gives  $\Delta H_f^\circ_{298}(\text{ZrC}_{1.00}) = -49.5$  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  $\text{MO}_x$ - $\text{MC}_y$ -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 ( $P_{\text{CO}}$ ) over  $\text{MO}_x$ - $\text{MC}_y$ -C-CO by the relations

$$(x/2) RT \ln P_{\text{O}_2} + RT \ln a_{\text{M}} = \Delta G^\circ_{\text{MO}_x} \quad (1)$$

where  $a(\text{MO}_x) = 1$

$$RT \ln P_{\text{CO}} + \Delta G^\circ_{\text{CO}} = \frac{1}{2} RT \ln P_{\text{O}_2} \quad (2)$$

and, therefore

$$RT \ln P_{\text{CO}} = -\Delta G^\circ_{\text{CO}} + (1/x)(\Delta G^\circ_{\text{MO}_x} - RT \ln a_{\text{M}}) \quad (3)$$

where  $\Delta G^\circ$  is the molar free energy of formation and  $a_{\text{M}}$  the activity of the metal in " $\text{MC}_y$ " in equilibrium with  $\text{MO}_x$  and C. If the metal activity  $a_{\text{M}}$  in " $\text{MC}_y$ " is approximately equal to  $a_{\text{M}}^\circ$  in the pure carbon-saturated  $\text{MC}_y$ , eq 3 reduces to

$$RT \ln P_{\text{CO}} = -\Delta G^\circ_{\text{CO}} + (1/x)(\Delta G^\circ_{\text{MO}_x} - \Delta G^\circ_{\text{MC}_y}) \quad (4)$$

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



We shall seek the condition for  $a_{\text{M}} = a_{\text{M}}^\circ$ . Assuming the carbon activity  $a_{\text{C}} = 1$  in the phase regions " $\text{MC}_y$ " + C and  $\text{MO}_x$  + " $\text{MC}_y$ " + C and " $\text{MC}_y$ " =  $\text{MC}_{y-\alpha}\text{O}_\beta$  in the latter region, the Gibbs-Duhem relation gives

$$\Delta G^\circ_{\text{MC}_{y-\alpha}\text{O}_\beta} = \Delta G^\circ_{\text{MC}_y} + \frac{1}{2} \int_0^\beta \Delta \bar{G}_{\text{O}_2} dz \quad (6)$$