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Amorphous/Crystalline (A/C) Thermodynamic “Rules of Thumb”: Estimating Standard Thermodynamic Data for Amorphous Materials Using Standard Data for Their Crystalline Counterparts

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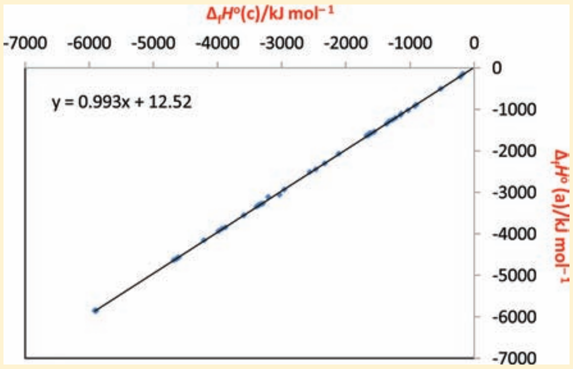
Supporting Information

ABSTRACT: Standard thermochemical data (in the form of $\Delta_f H^\circ$ and $\Delta_f G^\circ$) are available for crystalline (c) materials but rarely for their corresponding amorphous (a) counterparts. This paper establishes correlations between the sets of data for the two material forms (where known), which can then be used as a guideline for estimation of missing data. Accordingly, $\Delta_f H^\circ(\mathrm{a})/\mathrm{kJ\ mol^{-1}} \approx 0.993\Delta_f H^\circ(\mathrm{c})/\mathrm{kJ\ mol^{-1}} + 12.52$ ($R^2 = 0.9999$; $n = 50$) and $\Delta_f G^\circ/\mathrm{kJ\ mol^{-1}} \approx 0.988\Delta_f H^\circ(\mathrm{c})/\mathrm{kJ\ mol^{-1}} + 0.70$ ($R^2 = 0.9999$; $n = 10$). Much more tentatively, we propose that $S^\circ_{298}(\mathrm{c})/\mathrm{J\ K^{-1}\ mol^{-1}} \approx 1.084 S^\circ_{298}(\mathrm{c})/\mathrm{J\ K^{-1}\ mol^{-1}} + 6.54$ ($R^2 = 0.9873$; $n = 11$). An amorphous hydrate enthalpic version of the Difference Rule is also proposed (and tested) in the form $[\Delta_f H^\circ(\mathrm{M}_p\mathrm{X}_q\cdot n\mathrm{H_2O,a}) - \Delta_f H^\circ(\mathrm{M}_p\mathrm{X}_q\mathrm{,a})]/\mathrm{kJ\ mol^{-1}} \approx \Theta_{\mathrm{Hf}} n \approx -302.0n$, where $\mathrm{M}_p\mathrm{X}_q\cdot n\mathrm{H_2O}$ represents an amorphous hydrate and $\mathrm{M}_p\mathrm{X}_q$ the corresponding amorphous anhydrous parent salt.



1. INTRODUCTION

The tradition of making thermodynamic measurements on new inorganic crystalline systems has largely been abandoned. What is more, the situation for amorphous (or vitreous) materials systems (both traditional and novel) has always been poor, and only a handful of these have ever received any thermodynamic attention. The thermodynamics associated with amorphous phases of a material are not always easy to determine, and this is one of the reasons for the paucity of data found in standard thermochemical tables. The fact that the properties of such materials can depend, very much, on the mode of preparation and sample “history” perhaps offers some explanation of the situation.

Simple rules have always had their place in helping to unravel, simplify, and interpret the complex machinery of thermodynamics (Dulong−Petit, Neumann−Kopp, etc).[1] Accordingly, possession of “rules of thumb” that can offer a route into the likely thermodynamics is of obvious value. Over the past decade and a half, Jenkins and co-workers[2−5] have developed volume-based thermodynamics, a procedure whose aim is to simplify thermodynamics to the point where data at a useful level can easily be predicted and used, yet, because of its empirical nature, does not have the exactness and complete rigor customarily associated with thermodynamics. These procedures have been adopted widely across inorganic chemistry[6−9] to predict (usually successfully) various synthetic and chemical outcomes and afford a methodology enabling nonspecialist chemists to make thermodynamic assessments relatively easily with the help of nothing more than simple spreadsheets or even hand-held calculators. The Difference Rule,[10−13] employed here, emerges as yet another of these “volume-based” procedures presenting thermodynamic relationships that enable the representation of thermodynamic difference properties as a function of incremental integer additions, n, usually relating to homologous series or solvent additions. Thus, the thermodynamic properties, P, of a hydrate, $\mathrm{M}_p\mathrm{X}_q\cdot n\mathrm{H_2O}$, might emerge as a linear function of n or synonymously $V_m(\mathrm{M}_p\mathrm{X}_q\cdot n\mathrm{H_2O})$:

$$P(\mathrm{M_pX_q}.\ n\mathrm{L,c}) - P(\mathrm{M_pX_q,c}) = n\Theta P(\mathrm{c} - \mathrm{c}) \qquad (1)$$

where L can be $\mathrm{H_2O}$ or any other solvating ligand and $\Theta_P(\mathrm{c{-}c})$ is the rate of change of the Difference Function $[P(\mathrm{M}\ _p\mathrm{X}_q\cdot\ n\mathrm{L,c}) - P(\mathrm{M}_p\mathrm{X}_q\mathrm{,c})]$ with respect to n, the number of solvent molecules (L) present.

The aim of this paper is to draw attention to the fact that such data that do exist within standard thermochemical sources[14−18] exhibit a good linear correlation between the amorphous and crystalline phases (although, notably, this does not apply to amorphous elements[19]) therefore enabling us to then make estimates for missing data in cases where one or other is unavailable. It will usually be the case that only the *crystalline* value is available. The results presented here must be regarded tentatively and, at best, merely as “rules of thumb”. Although lacking the robustness and absolute rigor expected for thermodynamics, the need for such “rules” is considerable if we are to understand such diverse aspects of glass science as devitrification, the effects of thermal history, and the susceptibility to glass-in-glass phase separation or corrosion resistance. All of these factors influence the technology of formation and application of glasses, and so make this present study timely.

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In this paper, S.I. units are used throughout, all $\Delta_f H°$ and $\Delta_f G°$ values are quoted in kJ mol^{-1}, and all $S°_{298}$ values are in J K^{-1} mol^{-1}.

2. STANDARD ENTHALPY OF FORMATION DATA, $\Delta_f H°$

2.1. Procedure. Table 1 lists a series of available values of $\Delta_f H°(a)$/kJ mol^{-1} (tabulated as being either "amorphous" (a), "vitreous" (v), or "glass" (gl) within the original Circular 500 NBS database[14] or else the NBS source tables[15]), together with the corresponding $\Delta_f H°(c)$ for the crystalline counterpart. We shall use the term amorphous (a) from here on to include vitreous and glass. In Table 1, data are taken exclusively from ref 15 (apart from one piece of confirmatory data for SiO_2 from ref 21). Otherwise, we have avoided combining data for the amorphous and crystalline forms of a compound that originated from different compilations.

It is important that any observed correlation should be able to predict values that are within the reported errors of the data used to produce the correlation. The uncertainties arising in data appearing in ref 15 are stated to "depend on any inaccuracy in the total chain of reactions used to establish the value". Values are tabulated such that "the overall uncertainty lies between 8 and 80 units of the last (right-most) digit".[20] The obscurity of this statement probably reflects realism. The mineralogical databases[21,22] explicitly list uncertainties in values for both crystalline and amorphous data for all three thermodynamic quantities of interest. Examples of such values are given in Table 2. In each case, the percentage error is listed in parentheses. For individual materials for which multiple determinations have been made, parameters often exhibit quite a wide range of values (and associated errors). Thus, Borissova et al.[23] quote different values for $\Delta_f H°(Na_4P_2O_7,c)$, $\Delta_f H°(Zn_2P_2O_7,c)$, and $\Delta_f H°(Li_4P_2O_7,c)$ (Table 3) that differ by typically 2−4% with reported values for individual errors of 0.5−2.4%. More recent work suggests that experimental errors have remained at a fairly constant level over the years. Thus, the determination by O'Hare et al.[24] (Table 2) of the standard (298.15 K and 101.325 Pa) enthalpy of formation of crystalline and vitreous forms of GeS_2 leads to $\Delta_f H°(GeS_2,c) = -127.9 \pm 1.3$ (1.01%) and $\Delta_f H°(GeS_2,vit) = -115.4 \pm 1.6$ (1.38%). Therefore, we should ideally aim to produce "rules of thumb" that predict values to within 1% of (correct) experimental values.

It is difficult to make a comparison with errors arising from modeling/theoretical predictions because authors rarely visit this subject. Where calculations can be compared with experiment, they are frequently within or relatively close to the bounds of experimental uncertainty.

Figure 1 shows a plot of $\Delta_f H°(a)$ as the ordinate versus $\Delta_f H°(c)$ as the abscissa, which displays an excellent linear correlation ($R^2 = 0.9999$; $n = 50$ points) that takes the analytical form

$$\Delta_f H°(a) \approx 0.993\Delta_f H°(c) + 12.52 \quad (2)$$

This observation has not previously been reported. A previous study by Moiseev et al.[25] considered $\Delta_f H°(c)$ for crystalline materials, of interest as glass-forming systems, consisting of double oxides $A_xB_yO_z$ and investigated the dependence

$$\begin{aligned}\Delta_f H°(A_xB_yO_z,c) &= f(\Delta_f H°)\\ &= f[x_{AO}\Delta_f H°(AO,c) + x_{BO}\Delta_f H°(BO,c)]\end{aligned} \quad (3)$$

where, in this case, the standard enthalpies are defined with reference to the component oxides rather than the elements in their standard states and x_{AO} and x_{BO} are the mole fractions of oxides in double oxide $A_xB_yO_z$. What essentially these papers consider are the deviations of thermodynamic data from the ideal relationship (3), and the discussions are very much related to the double oxide Difference Rule used below. Specific studies[26−29] on silicate glasses and melts relate to much higher temperatures than ambient.

Relationship (2) offers us a convenient means of obtaining rough estimates of $\Delta_f H°(a)$ for amorphous materials in cases where only the crystalline $\Delta_f H°(c)$ value is known, the more usual situation.

In Table 1, it should be noted that, in cases where more than one polymorph exists for the crystalline phase, the most stable polymorph at room temperature has been included in column 2, although, in many systems, the structure of a glass is thought to be more closely related to that of any high-temperature polymorph. It is quite surprising, in the case of B_2O_3, that the correlation works so well in view of the quite different structures exhibited by the crystalline and amorphous forms and indicates the dominant influence of the short-range structure rather than the medium-range structure. The view is generally held that compounds that readily form glasses have several energetically similar crystal polymorphs.

Table 4 lists $\Delta_f H°(c)$ data for a number of materials not included in the original data analysis and retained as a "test" set. This includes the mineral $Ca_{12}Al_{14}O_{33}$ (=$12CaO\cdot7Al_2O_3$), which has, because of its formula unit, the largest tabulated value of $\Delta_f H°(a)$, being 4−5 times the magnitude of that for any other amorphous materials listed in the NBS table.[15] This datum could have been included in Figure 1 and our analysis but would, because of its magnitude, form one of the extrema of the data and would have (unjustifiably) "weighted" the linear regression. A preferable procedure (adopted) is to exclude this datum from the analysis but to check later its conformity with the remaining points, as is done in Table 2.

2.2. Effectiveness of the Rule. Column 6 of Table 1 shows the success in predicting the amorphous values of $\Delta_f H°(a)$ using eq 2 from the crystalline values found in column 2. Column 7 shows the percentage error, which is, in the vast majority (96%) of the cases, less than 2%, which compares well with the experimental errors (72% of the predicted values are within the desired 1% of the observed values; a full cumulative list is given in Table 5). Here, for the sulfides (MnS and Sb_2S_3), the prediction errors are considerably larger (6.7% and 12.4%) than those for the other materials, suggesting that sulfides are not well represented by the correlation or that the NBS literature values[15] for $\Delta_f H°(a)$ may be suspect and a redetermination may be advisible. Other crystalline data, taken from a number of sources and given in Table 4, are employed as a test set for eq 2, where errors (column 7) of less than 1.6% are reported for the predictions (8 out of the 11 values are within 1% of the experimental value). Of the two experimental values of $\Delta_f H°(Na_2ZnP_2O_7,c)$ cited in Table 4, our correlation suggests that −2863.8 is the more accurate experimental value.[23]

2.3. Hydrated Materials and Hydrate Difference Rule (HDR). Concerning ourselves now with the enthalpy data for *hydrated salts*, the NBS database[15] cites $\Delta_f H°(Mn(NO_3)_2,c) = -576.26$ kJ mol^{-1} for the anhydrous salt and $\Delta_f H°(Mn(NO_3)_2\cdot6H_2O,a) = -2371.9$ kJ mol^{-1} for the amorphous form of the corresponding hexahydrate. The HDR[10−13] takes the form

$$\begin{aligned}&\Delta_f H°(M_pX_q\cdot nH_2O,c)\\ &\quad\approx \Delta_f H°(M_pX_q,c) + n\Theta_{Hf}(H_2O,c-c)\end{aligned} \quad (4)$$

Table 1. Tabulated Data of $\Delta_f H°(c)$ and $\Delta_f H°(a)$ for a Range of Materials (NBS Refers to the Thermochemical Tabulation in Reference 15)[a]

material	$\Delta_f H°(c)/\mathrm{kJ\ mol^{-1}}$	ref	$\Delta_f H°(a)/\mathrm{kJ\ mol^{-1}}$	ref	$\Delta_f H°(a)/\mathrm{kJ\ mol^{-1}}$ from eq2	% error
Silicates						
$PbSiO_3 = PbO\cdot SiO_2$	−1145.7	NBS	−1137.6	NBS	−1125.9	1.0
$Pb_2SiO_4 = 2PbO\cdot SiO_2$	−1363.1	NBS	−1348.1	NBS	−1341.8	0.5
$MnSiO_3 = MnO\cdot SiO_2$	−1320.9	NBS	−1285.3	NBS	−1299.9	−1.1
$CaSiO_3 = CaO\cdot SiO_2$	−1634.94	NBS	−1601.01	NBS	−1611.8	−0.7
$CaAl_2Si_2O_8 = CaO\cdot Al_2O_3\cdot 2SiO_2$	−4209.5	NBS	−4155.1	NBS	−4169.1	−0.3
$Ca_2Al_2Si_2O_8 = 2CaO\cdot Al_2O_3\cdot 2SiO_2$	−3981.5	NBS	−3931.7	NBS	−3942.7	−0.3
$CaMgSi_2O_6 = CaO\cdot MgO\cdot 2SiO_2$	−3206.5	NBS	−3113	NBS	−3172.9	−1.9
$Ca_2MgSi_2O_7 = 2CaO\cdot MgO\cdot 2SiO_2$	−3877.19	NBS	−3844.7	NBS	−3839.1	0.1
$SrSiO_3 = SrO\cdot SiO_2$	−1633.9	NBS	−1590	NBS	−1610.8	−1.3
$BaSiO_3 = BaO\cdot SiO_2$	−1623.6	NBS	−1573	NBS	−1600.6	−1.8
$Li_2SiO_3 = Li_2O\cdot SiO_2$	−1648.1	NBS	−1628	NBS	−1624.9	0.2
$Li_2Si_2O_5 = Li_2O\cdot 2SiO_2$	−2559.8	NBS	−2512.5	NBS	−2530.5	−0.7
$Na_2SiO_3 = Na_2O\cdot SiO_2$	−1554.9	NBS	−1540.1	NBS	−1532.3	0.5
$Na_2Si_2O_5 = Na_2O\cdot 2SiO_2$	−2467.7	NBS	−2445.8	NBS	−2439.0	0.3
$NaAlSi_3O_8 = {}^1/_2Na_2O\cdot {}^1/_2Al_2O_3\cdot 3SiO_2$	−3925.8	NBS	−3875.2	NBS	−3887.3	−0.3
$KAlSi_3O_6 = {}^1/_2K_2O\cdot {}^1/_2Al_2O_3\cdot 2SiO_2$	−3034.2	NBS	−3058.1	NBS	−3001.7	1.8
$Na_{0.7794}K_{0.2206}AlSiO_4$	−2109.6	NBS	−2071.9	NBS	−2083.3	−0.6
Oxides						
MnO_2	−520.03	NBS	−502.5	NBS	−504.4	−0.4
$CaAl_2O_4 = CaO\cdot Al_2O_3$	−2326.3	NBS	−2301	NBS	−2298.6	0.1
$Ca_2Al_2O_5 = 2CaO\cdot Al_2O_3$	−2958	NBS	−2933	NBS	−2926.0	0.2
$Ca_3Al_2O_6 = 3CaO\cdot Al_2O_3$	−3587.8	NBS	−3552	NBS	−3551.6	0.0
SiO_2 quartz	−910.94	NBS	−903.49	NBS	−892.4	1.2
SiO_2 quartz	−910.7	19	−903.2	19	−892.7	1.2
Al_2O_3	−1675.7	NBS	−1632	NBS	−1652.3	−1.2
UO_3	−1217.5	NBS	−1208.3	NBS	−1203.5	0.4
Borates						
B_2O_3	−1272.77	NBS	−1254.53	NBS	−1252.1	0.2
$Na_2B_4O_7 = Na_2O\cdot 2B_2O_3$	−3291.1	NBS	−3271.1	NBS	−3256.9	0.4
$Na_2B_6O_{10} = Na_2O\cdot 3B_2O_3$	−4603.2	NBS	−4569.8	NBS	−4560.2	0.2
$Na_2B_8O_{13} = Na_2O\cdot 4B_2O_3$	−5912	NBS	−5853	NBS	−5860.2	−0.1
$Li_2Na_2B_2O_5 = Li_2O\cdot Na_2O\cdot B_2O_3$	−4680.2	NBS	−4633.8	NBS	−4636.7	−0.1
$LiNaB_4O_7 = {}^1/_2Li_2O\cdot {}^1/_2Na_2O\cdot 2B_2O_3$	−3342.93	NBS	−3297.79	NBS	−3308.4	−0.3
$LiNaB_6O_{10} = {}^1/_2Li_2O\cdot {}^1/_2Na_2O\cdot 3B_2O_3$	−4629.93	NBS	−4587.5	NBS	−4586.8	0.0
$LiNaB_8O_{13} = {}^1/_2Li_2O\cdot {}^1/_2Na_2O\cdot 4B_2O_3$	−5900.57	NBS	−5851.87	NBS	−5848.9	0.1
$Li1\cdot 5Na^1/_2B_4O_7 = {}^3/_4Li_2O\cdot {}^1/_4Na_2O\cdot 2B_2O_3$	−3353.94	NBS	−3315.19	NBS	−3319.3	−0.1
$Li_{1.5}Na^1/_2B_4O_7 = {}^3/_4Li_2O\cdot {}^1/_4Na_2O\cdot 3B_2O_3$	−4641.48	NBS	−4603.4	NBS	−4598.2	0.1
$Li_{1.5}Na^1/_2B_8O_{13} = {}^3/_4Li_2O\cdot {}^1/_4Na_2O\cdot 4B_2O_3$	−5893.37	NBS	−5858.06	NBS	−5841.7	0.3
$Na_{1.5}Li^1/_2B_4O_7 = {}^1/_4Li_2O^3/_4Na_2O\cdot 2B_2O_3$	−3318.87	NBS	−3281.39	NBS	−3284.5	−0.1
$Na_{1.5}Li^1/_2B_6O_{10} = {}^1/_4Li_2O\cdot {}^3/_4Na_2O\cdot 3B_2O_3$	−4617.88	NBS	−4575.66	NBS	−4574.8	0.0
$Na_{1.5}Li^1/_2B_8O_{13} = {}^1/_4Li_2O\cdot {}^3/_4Na_2O\cdot 4B_2O_3$	−5894.84	NBS	−5848.1	NBS	−5843.2	0.1
$CaB_4O_7 = CaO\cdot 2B_2O_3$	−3360.25	NBS	−3307.37	NBS	−3325.6	−0.6
$Li_2B_4O_7 = Li_2O\cdot 2B_2O_3$	−3390.3	NBS	−3342.2	NBS	−3355.4	−0.4
$Li_2B_6O_{10} = Li_2O\cdot 3B_2O_3$	−4680.2	NBS	−4633.8	NBS	−4636.7	−0.1
Hydrates						
$NiSeO_3\cdot 2H_2O$	−1134.32	NBS	−1106.2	NBS	−1114.6	−0.8
$MgSO_4\cdot H_2O$	−1602.1	NBS	−1574.9	NBS	−1579.2	−0.3
Others						
$MgSeO_3 = MgO\cdot SeO_2$	−900.19	NBS	−892.66	NBS	−882.0	1.2
$Be(OH)_2$	−902.5	NBS	−897.9	NBS	−884.3	1.5
$Mg(OH)_2$	−924.54	NBS	−920.5	NBS	−906.2	1.6
BeF_2	−1026.8	NBS	−1022.2	NBS	−1007.8	1.4
MnS	−214.2	NBS	−213.8	NBS	−200.6	6.2
Sb_2S_3	−174.9	NBS	−143.7	NBS	−161.6	−12.4

[a] An error in the NIST database[18] assigns identical values of $\Delta_f H°/\mathrm{kJ\ mol^{-1}}$ to $SiO_2(c)$ and $SiO_2(a)$.

in which the constant $\Theta_{Hf}(H_2O,c\text{—}c)$ has the value −298.6 kJ mol^{-1} for any general hydrate $M_pX_q\cdot nH_2O$. Using this rule, we can predict that $\Delta_f H°(Mn(NO_3)_2\cdot 6H_2O,c)$ should be approximately −2367.9 kJ mol^{-1}. Further, using eq 2, $\Delta_f H°(Mn(NO_3)_2,a)$ is

Table 2. Examples of Explicitly Quoted Uncertainties on Thermodynamic Values Reported in a Mineralogical Database[21] and by O'Hare et al.[24] That Represent Very High Quality Data

		error			error	
	crystalline	±	%	amorphous	±	%
		$NaAlSi_3O_8$[21]				
$\Delta_f H°$ (kJ mol^{-1})	−3924.24	3.64	0.09	−3875.40	3.70	0.10
$\Delta_f G°$ (kJ mol^{-1})	−3706.507	3.640	0.10	−3665.330	3.720	0.10
$S°$ (J K^{-1} mol^{-1})	226.40	0.40	0.18	251.90	1.50	0.60
		$KAlSi_3O_8$[21]				
$\Delta_f H°$ (kJ mol^{-1})	−3959.56	3.37	0.08	−3914.74	3.37	0.09
$\Delta_f G°$ (kJ mol^{-1})	−3739.776	3.400	0.09	−3703.513	3.500	0.10
$S°$ (J K^{-1} mol^{-1})	232.90	0.48	0.21	261.60	1.78	0.68
		$CaAl_2Si_2O_8$[21]				
$\Delta_f H°$ (kJ mol^{-1})	−4243.040	3.125	0.07	−4171.28	3.30	0.08
$\Delta_f G°$ (kJ mol^{-1})	−4017.266	3.145	0.08	−3956.836	3.320	0.08
$S°$ (J K^{-1} mol^{-1})	199.30	0.30	0.15	237.30	2.50	1.05
		GeO_2[21]				
$\Delta_f H°$ (kJ mol^{-1})	−551.03	0.80	0.14	−526.35	0.63	0.12
$\Delta_f G°$ (kJ mol^{-1})	−497.074	0.900	0.19	−475.180	0.710	0.15
$S°$ (J K^{-1} mol^{-1})	55.27	0.27	0.49	64.50	0.30	0.47
		GeS_2[24]				
$\Delta_f H°$ (kJ mol^{-1})	−127.9	1.3	1.01	−115.4	1.6	1.38

Table 3. Uncertainties Quoted by Borissova et al. from the Literature for Pyrophosphates, Indicating the Individual Reported Errors and Standard Deviations (stdev) on the Means of the Values

	$\Delta_f H°$(c) (kJ mol^{-1})[a]	error (±kJ mol^{-1})	error (±%)
$Na_4P_2O_7$,	−854.9[30]	4.0	0.47
	−854.3		
	−881.2[31]	10.0	1.13
	−876.0[23]	4.0	0.46
	stdev = 1.6%		
$Zn_2P_2O_7$	−327.9[31]	8.0	2.44
	−342.1[23]	2.5	0.73
	stdev = 3%		
$Li_4P_2O_7$	−673.2[31]	7.5	1.11
	−685.5[23]	4.0	0.58
	stdev = 1.3%		

[a] Enthalpies of formation from the constituent oxides.

predicted to be −559.7 kJ mol^{-1} using the data for the crystalline anhydrous salt. Assuming now the existence of an analogous amorphous Difference Rule of the form

$$\Delta_f H°(M_pX_q{\cdot}nH_2O,a) \approx \Delta_f H°(M_pX_q,a) + n\Theta_{Hf}(H_2O,a{-}a) \qquad (5)$$

$\Theta_{Hf}(H_2O,a{-}a)$ then takes the value −302.0 kJ mol^{-1}. We can test this tentative new rule to *predict* a value for amorphous $\Delta_f H°(Be(OH)_2{\cdot}0.75H_2O,a)$ (known experimentally[15] to have the value −1116.7 kJ mol^{-1}). Taking $n = 0.75$ and using $\Delta_f H°(Be(OH)_2,a) = -897.9$ kJ mol^{-1} as experimentally determined[15] for freshly precipitated material, coupled with the above value of $\Theta_{Hf}(H_2O,a{-}a)$, eq 5 leads to the prediction that $\Delta_f H°(Be(OH)_2{\cdot}0.75H_2O,a) \approx -1124.4$ kJ mol^{-1}, so returning an error of only 0.7%.

The above examples test the basis of the "rule of thumb" established for standard enthalpy data.

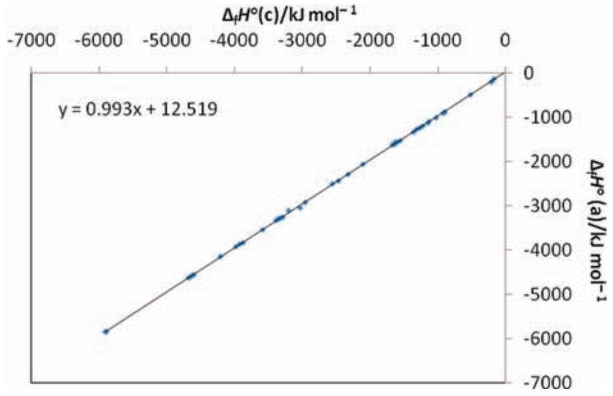

Figure 1. Plot of $\Delta_f H°$(a) as the ordinate versus $\Delta_f H°$(c) as the abscissa for a range of materials ($R^2 = 0.999$; $n = 50$).

2.4. Existence of Difference Rules in the Case of Crystalline and Amorphous Double Oxides, $Al_2O_3{\cdot}nCaO$.

Tables 1 and 2 contain $\Delta_f H°$ data for the crystalline and amorphous forms of the double oxides, $nCaO{\cdot}Al_2O_3$(c) (n = 1−3). If we regard these double oxides as being solid solutions in which one oxide is "solvating" the other, then we can conceive of their treatment using a form of the Difference Rule.[10−13] If we consider first the oxide Al_2O_3(c) as the "parent" oxide (n = 0) with n "solvent" CaO molecules attached, then we can propose the possible existence of a "Difference Rule" in the form

$$[\Delta_f H°(Al_2O_3{\cdot}nCaO,c)] - \Delta_f H°(Al_2O_3,c) \approx n(CaO)\ \Theta_{Hf}(CaO,c{-}c) \qquad (6)$$

A plot (constrained to pass through the origin) of the data in Table S1 and Figure S1 (Supporting Information, SI) tests this idea and yields

$$\Delta_f H°(Al_2O_3{\cdot}nCaO,c) - \Delta_f H°(Al_2O_3,c) \approx n(CaO)\ \Theta_{Hf}(CaO,c{-}c) \approx -639.8n(CaO) \quad \text{kJ mol}^{-1} \qquad (7)$$

Table 4. Tabulated Experimental Data of $\Delta_f H°(c)$ and $\Delta_f H°(a)$ As Predicted by Substitution of the Experimental Values of $\Delta_f H°(c)$ in eq 2 for a Range of Materials

material	$\Delta_f H°(c)$/kJ mol^{-1}	ref	$\Delta_f H°(a)$/kJ mol^{-1}	ref	$\Delta_f H°(a)$/kJ mol^{-1} from eq 2	% error
			Test Data			
GeS_2	−127.9 ± 1.3	24	−115.4 ± 1.6	24	−114.4	0.8
$Zn(PO_3)_2$	−2083.2	NBS	−2030.5	NBS	−2056.1	1.3
$Na_3P_3O_9$	−3653	NBS	−3623.2	NBS	−3614.9	0.2
$Ca_{12}Al_{14}O_{33} = 12CaO{\cdot}7Al_2O_3$	−19430	NBS	−19087	NBS	−19281.5	−1.0
$MgSeO_3 = MgO{\cdot}SeO_2$	−900.19	NBS	−892.6	NBS	−881.4	1.3
$Zn_2P_2O_7$	−2530.7	23	−2478.7	23	−2500.5	−0.9
$Na_2ZnP_2O_7$	−2900.7	23	−2844.3	23	−2867.9	−0.8
$Na_2ZnP_2O_7$	−2900.7	23	−2863.8	23	−2867.9	−0.1
$KAlSi_3O_8 = {}^1/_2K_2O{\cdot}{}^1/_2Al_2O_3{\cdot}3SiO_2$	−3959.56 ± 3.37	21	−3914.74 ± 3.37	21	−3919.3	−0.1
$CaAl_2Si_2O_8 = CaO{\cdot}Al_2O_3{\cdot}2SiO_2$	−4243.040 ± 3.125	21	−4174.28 ± 3.30	21	−4200.8	−0.6
GeO_2	−551.03 ± 0.80	21	−526.35 ± 0.63	21	−534.7	−1.6

Table 5. Cumulative Occurrence of Errors between the Experimental Values of $\Delta_f H°(a)$ and Those Calculated Using Equation 2

maximum % error	cumulative occurrence/%	maximum % error	cumulative occurrence/%
0	6	1.25	82
0.25	34	1.5	88
0.5	60	1.75	90
0.75	68	2	96
1	72	>2	100

for which $R^2 = 0.9999$ and $n = 5$. Figure S1 in the SI shows a plot of the difference function, $[\Delta_f H°(Al_2O_3.nCaO,c) - \Delta_f H°(Al_2O_3,c)]$, versus n using the data from Tables 1 and 2. A corresponding plot for the amorphous solids, using data from Tables 1 and 2 (Table S2 and Figure S2 in the SI), takes the form ($R^2 = 0.9995$; $n = 5$):

$$\Delta_f H°(Al_2O_3{\cdot}nCaO,a) - \Delta_f H°(Al_2O_3,a) \approx n(CaO)\ \Theta_{Hf}(CaO,a{-}a) \approx -644n(CaO) \quad \text{kJ mol}^{-1} \tag{8}$$

Both of these plots confirm the existence of the equivalent of a Difference Rule for these solid double oxide materials.

Alternatively, we can regard the same compounds of the general type $nCaO{\cdot}Al_2O_3$ as being the equivalent of n molecules having the formula $CaO{\cdot}1/nAl_2O_3$, whose standard enthalpy of formation, $\Delta_f H°(CaO{\cdot}1/nAl_2O_3,c \text{ or } a)$ can be obtained by dividing $\Delta_f H°(Al_2O_3{\cdot}nCaO,c \text{ or } a)$, equivalent to $\Delta_f H°(nCaO{\cdot}Al_2O_3,c \text{ or } a)$, by n. Here we can conceive of the possible existence of Difference Rules of the forms

$$\Delta_f H°(CaO{\cdot}1/nAl_2O_3,c) - \Delta_f H°(CaO,c) \approx 1/n(Al_2O_3)\ \Theta_{Hf}(Al_2O_3,c{-}c) \quad \text{kJ mol}^{-1} \tag{9}$$

or

$$\Delta_f H°(CaO{\cdot}1/nAl_2O_3,a) - \Delta_f H°(CaO,a) \approx 1/n(Al_2O_3)\ \Theta_{Hf}(Al_2O_3,a{-}a) \quad \text{kJ mol}^{-1} \tag{10}$$

Tables S3 and S4 (SI) list the available data for crystalline and amorphous $CaO{\cdot}1/nAl_2O_3$ double oxides and confirm, from the observed graph (Figure S3 in the SI), the perfect linearity ($R^2 = 1$; $n = 5$) of the plot of the difference function, $[\Delta_f H°(CaO{\cdot}1/nAl_2O_3,c) - \Delta_f H°(CaO,c)]$ versus $[1/n(Al_2O_3)]$, with the existence of a *crystalline* version of the Difference Rule, eq 9, having the analytical form

$$\Delta_f H°(CaO{\cdot}1/nAl_2O_3,c) - \Delta_f H°(CaO,c) \approx 1/n(Al_2O_3)\ \Theta_{Hf}(Al_2O_3,c{-}c) \approx -1703.3[1/n(Al_2O_3)] \quad \text{kJ mol}^{-1} \tag{11}$$

Because, even though $\Delta_f H°(CaO,c)$ is known (−635.089 ± 0.879 kJ mol^{-1}),[21], no experimental data are available for its amorphous counterpart, $\Delta_f H°(CaO,a)$, we cannot evaluate the difference function, $[\Delta_f H°(CaO{\cdot}1/nAl_2O_3,a) - \Delta_f H°(CaO,a)]$ (see Table S4 in the SI). Instead, rearrangement of the proposed eq 10 leads us to

$$[\Delta_f H°(CaO{\cdot}1/nAl_2O_3,a)] \approx [1/n(Al_2O_3)]\Theta_{Hf}(Al_2O_3,a{-}a) + \Delta_f H°(CaO,a) \quad \text{kJ mol}^{-1} \tag{12}$$

indicating that, if the Difference Rule (of the form of eq 10) was indeed valid for the amorphous double oxide, then a plot of $\Delta_f H°(CaO{\cdot}1/nAl_2O_3,a)$ versus $1/n$ should also be linear with gradient $\Theta_{Hf}(Al_2O_3,a{-}a)$ and offset $\Delta_f H°(CaO,a)$. The relevant plot is displayed in Figure S4 in the SI, for which $R^2 = 0.9998$ and $n = 4$, leading to the analytical form

$$[\Delta_f H°(CaO{\cdot}1/nAl_2O_3,a)] \approx -1674[1/n(Al_2O_3)] - 623 \text{ kJ mol}^{-1} \tag{13}$$

whereupon

$$\Delta_f H°(CaO,a) \approx -623 \text{ kJ mol}^{-1} \tag{14}$$

This value can now be compared with that obtained using the known value of $\Delta_f H°(CaO,c)$ in eq 2. By this route, we obtain the estimate

$$\Delta_f H°(CaO,a) \approx -618.1 \text{ kJ mol}^{-1} \tag{15}$$

and the close agreement of these two predictions for $\Delta_f H°(CaO,a)$, lying as they do within 0.8% (or 5 kJ mol^{-1}) of each other, confirms the existence of a Difference Rule of the form of eq 10 and the satisfactory nature of our correlation (2) as well as provides a value for the standard heat of formation of a material that is very difficult to synthesize experimentally.

Table 6. Tabulated Data of $\Delta_f G°$(c) and $\Delta_f G°$(a) for a Range of Materials (NBS Refers to the Thermochemical Tabulation in Reference 15)

material	$\Delta_f G°$(c)/kJ mol^{-1}	ref	$\Delta_f G°$(a)/kJ mol^{-1}	ref	$\Delta_f G°$(a)/kJ mol^{-1} from eq 6	% error
Silicates						
SiO_2 α-quartz	−856.64	NBS	−850.7	NBS	−845.3	0.6
SiO_2 α-quartz	−856.288 ± 1.100	21	−850.559 ± 2.134	21	−845.0	0.7
$CaAl_2Si_2O_8 = CaO{\cdot}Al_2O_3{\cdot}2SiO_2$ anorthite, hexagonal	−4002.3	NBS	−3940.8	NBS	−3952.0	−0.3
$CaAl_2Si_2O_8 = CaO{\cdot}Al_2O_3{\cdot}2SiO_2$ anorthite, hexagonal	−4017.266 ± 3.145	21	−3956.836 ± 3.320	21	−3966.75	−0.3
$NaAlSi_3O_8 = {}^1/_2Na2O{\cdot}{}^1/_2Al_2O_3{\cdot}3SiO_2$ low albite	−3711.5	NBS	−3665.1	NBS	−3664.8	0.0
$NaAlSi_3O_8 = {}^1/_2Na_2O{\cdot}{}^1/_2Al_2O_3.3SiO_2$ analbite	−3706.507 ± 3.660	21	−3665.330 ± 3.720	21	−3659.9	0.1
Borates						
B_2O_3	−1193.65	NBS	−1182.3	NBS	−1178.15	0.4
$Na_2B_4O_7 = Na_2O{\cdot}2B_2O_3$	−3096	NBS	−3076.8	NBS	−3056.9	0.6
Hydrates						
$MgSO_4{\cdot}H_2O$	−1428.7	NBS	−1404.9	NBS	−1410.3	−0.4
Oxides						
GeO_2	−497.074 ± 0.900	21	−475.180 ± 0.710	21	−490.2	−3.1

Table 7. Tabulated Experimental Data of $\Delta_f G°$(c) and $\Delta_f G°$(a) As Predicted by Substitution of the Experimental Values of $\Delta_f G°$(c) in eq 6 for a Range of Materials (NBS and KK Refer to the Thermochemical Tabulations in References 15 and 17, Respectively)

material	$\Delta_f G°$(c)/kJ mol^{-1}	ref	$\Delta_f G°$(a)/kJ mol^{-1}	ref	$\Delta_f G°$(a)/kJ mol^{-1} from eq 6	% error
$CaAl_2O_4 = CaO{\cdot}Al_2O_3$	−2208.7	NBS	−2169.4	KK	−2174.2	−0.2
$Ca_2Al_2O_5 = 2CaO{\cdot}Al_2O_3$	−2807	KK	−2769.4	KK	−2769.4	0.1
$Ca_2B_2O_5 = 2CaO{\cdot}B_2O_3$	−2596.59	NBS	?		−2588.3	
$CaB_4O_7 = CaO{\cdot}2B_2O_3$	−3167.01	NBS	−3095.7	KK	−3123.2	−0.9
$Ca_3Al_2O_6 = 3CaO{\cdot}Al_2O_3$	−3436.3	KK	−3380.3	KK	−3389.8	−0.3
$Ca_3Al_2O_6 = 3CaO{\cdot}Al_2O_3$	−3411.5	NBS	−3381.9	KK	−3365.3	0.5
$Ca_3Al_2O_6 = 3CaO{\cdot}Al_2O_3$	−3436.3	KK	−3381.9	KK	−3389.8	−0.2
$Ca_3Al_2O_6 = 3CaO{\cdot}Al_2O_3$	−3411.5	NBS	−3380.3	KK	−3365.3	0.5
$PbSiO_3 = PbO{\cdot}SiO_2$	−1062.1	NBS	−1000.8	KK	−1038.9	−3.8
$PbSiO_3 = PbO{\cdot}SiO_2$	−1030.5	25	−1000.8	KK	−1007.6	−0.7
$Pb_2SiO_4 = 2PbO{\cdot}SiO_2$	−1252.6	NBS	−1211.3	KK	−1227.5	−1.3
$Al(OH)_3$	−1149.8	KK	−1137.6	KK	−1132.5	1.0
$CdCO_3$	−683.5	KK	−666.5	KK	−664.0	0.4

The work of Moiseev et al.[25] is very pertinent here, in that it is effectively based on the existence of deviations from the leading term in the Difference Rule, as stated in eq 1 adapted to the compounds found in Table 1 of ref 25, where $P = \Delta_f H°$ and M_pX_q and L are variously the component salts, as listed in the table.

3. STANDARD FREE ENERGY OF FORMATION DATA, $\Delta_F G°$

Gibbs energy of formation data have, in fact, been established for relatively few amorphous materials within the NBS database,[15] although some supplementary data are available from Russian sources.[17] The former data are used to examine the existence of a linear correlation (see Table 6), while the latter data are used as a "test" set (see Table 7). Table 6 lists $\Delta_f G°$(a)/kJ mol^{-1} and $\Delta_f G°$(c) data for amorphous and crystalline pairs of materials taken exclusively from refs 15 and 21. Figure 2 shows a plot of $\Delta_f G°$(a) versus $\Delta_f G°$(c), which displays an excellent linear correlation ($R^2 = 0.9999$; $n = 10$ points), which takes the analytical form

$$\Delta_f G°(\mathrm{a}) \approx 0.988\Delta_f G°(\mathrm{c}) + 0.70 \quad \mathrm{kJ\ mol^{-1}} \tag{16}$$

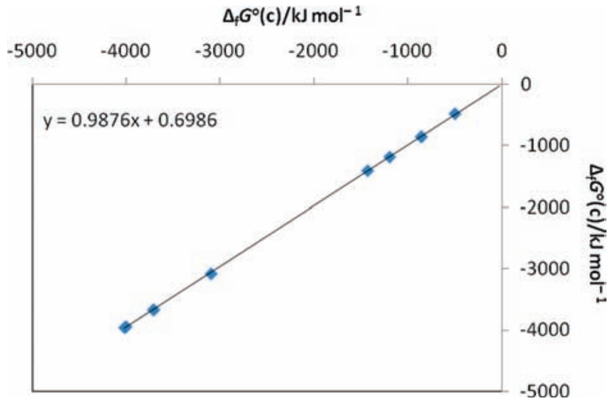

Figure 2. Plot of $\Delta_f G°$(a) versus $\Delta_f G°$(c) for a range of materials ($R^2 = 1.000$; $n = 10$).

Table 7 takes data from mixed sources[15,17,25] (avoided in Table 6) and uses these data to test the success achieved by using $\Delta_f G°$(c) in eq 16 in order to predict $\Delta_f G°$(a) (column 6), which can then be compared with the experimental value (column 4). Column 7 then provides the percentage errors, which from Tables 6 and 7 are seen to be only in two cases greater than 2.4%. Table 7 shows that the predicted $\Delta_f G°$(a) data for the listings have errors of less than 1.3% except in the cases of the lead silicates. The NBS database[15] displays no entries for either amorphous $PbSiO_3$ or Pb_2SiO_4, but Table 7 includes two disparate entries for crystalline $PbSiO_3$ one of

Table 8. Tabulated Data of $S°_{298}$(c) and $S°_{298}$(a) for a Range of Materials (NBS Refers to the Thermochemical Tabulation in Reference 15)[a]

material	$S°_{298}$(c)/J K $^{-1}$ mol^{-1}	ref	$S°_{298}$(a)/J K $^{-1}$ mol^{-1}	ref	$S°$(a)/J K^{-1} mol^{-1} from eq 8	% error
Silicates						
$CaAl_2Si_2O_8 = CaO{\cdot}Al_2O_3{\cdot}2SiO_2$	199.30 ± 0.30	21	237.30 ± 2.50	21	222.6	6.2
$KAlSi_3O_8 = {}^1/_2K_2O{\cdot}{}^1/_2Al_2O_3{\cdot}3SiO_2$	232.90 ± 0.48	21	261.60 ± 1.78	21	259.1	1.0
$NaAlSi_3O_8 = {}^1/_2Na_2O{\cdot}{}^1/_2Al_2O_3{\cdot}3SiO_2$	226.40 ± 0.40	21	251.90 ± 1.50	21	252.0	−0.1
$PbSiO_3 = PbO{\cdot}SiO_2$	109.6	NBS	126.3	KK	125.4	0.7
Borates						
B_2O_3	54.0	NBS	77.8	NBS	65.1	16.3
$Na_2B_4O_7 = Na_2O{\cdot}2B_2O_3$	189.5	NBS	192.9	NBS	212.0	−9.9
Hydrate						
$MgSO_4{\cdot}H_2O$	126.4	NBS	138.1	NBS	143.6	−4.0
Oxides						
SiO_2	41.46	21	77.8	21	51.5	−8.6
SiO_2	41.84	NBS	46.9	NBS	51.9	−10.7
GeO_2	55.27	21	64.50	21	66.5	−3.1
As_2O_3	107.1	NBS	127.6	KK	122.7	3.9

[a] In some situations, where the entropy of an amorphous material is known but the corresponding crystalline value is absent, a reviewer has pointed out that one way to proceed would be to estimate the crystalline value. This could be done by using Latimer's rules,[32] Glasser and Jenkins tabulated single-ion entropy values,[33] or Jenkins and Glasser's entropy–volume equation,[34] so providing three estimates of the crystalline data that could then be entered into the correlation above.

which, from ref 25, gives excellent agreement, via eq 16, with the only known amorphous value from ref 17, although the agreement for Pb_2SiO_4 is less satisfactory. If the 22 pairs of data from Tables 6 and 7 are combined and plotted, the correlation coefficient (R^2 = 0.9999; n = 22) is identical with that for the Table 6 correlation (R^2 = 0.9999; n = 10), with the fit taking the form

$$\Delta_f G°(a) \approx 0.990\Delta_f G°(c) + 12.81 \text{ kJ mol}^{-1} \quad (17)$$

and the prediction errors are marginally worsened (in the case of the extended data set (n = 22): 1.8% ≥ [error] ≥ −3.8% compared to the training set (n = 10) for which 0.7% ≥ [error] ≥ −3.2%). It is notable that the linear parameters of eq 17 for the extended data set are more closely similar to those of eq 2 than are the parameters of eq 6, as may possibly be anticipated.

4. STANDARD ENTROPY DATA, $S°$

Paucity of data makes only 11 pairs of $S°_{298}$ data available to study any relationship (linear or otherwise) that might exist between the absolute standard entropy, $S°_{298}$, of the amorphous and crystalline forms. Despite this, what limited data there are in NBS[15] and Robie et al.[21] suggest that an (approximate) linear form of the correlation may exist.

The standard entropy $S°_{298}$(c) values recorded in refs 15 and 21, for the materials listed in Table 8, have been plotted versus $S°_{298}$(a) at 298 K and give rise to the following linear fit with parameters (R^2 = 0.9873; n = 11):

$$S°_{298}(a) \approx 1.084S°_{298}(c) + 6.54 \text{ J K}^{-1} \text{ mol}^{-1} \quad (R^2 = 0.9873;\ n = 11) \quad (18)$$

As would be anticipated, the more disordered material (i.e., the amorphous phase) has the higher entropy value in all cases. This gives rise to the gradient of the correlation, which, being greater than 1.0 in relationship (17), ensures that $S°_{298}(a) > S°_{298}(c)$. Figure 3 displays a plot of the data assembled, from which it is seen that there is considerable spread of points and a much lower correlation coefficient, in stark contrast to the almost perfect correlations (R^2 = 0.9999) of the enthalpy (Figure 1) and Gibbs energy plots (Figure 2).

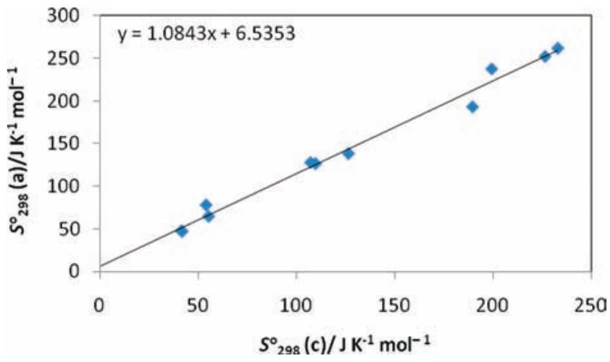

Figure 3. Plot of $S°_{298}$(a) versus $S°_{298}$(c) for a limited range of materials for which the standard entropy is recorded (R^2 = 0.9873; n = 11).

Attempts to replicate the standard entropy data for the known experimental values $S°_{298}(SiO_2,a)$ = 46.9[15] or 47.40[21] J K^{-1} mol^{-1} and $S°_{298}(As_2O_3,a)$ = 127.6[17] J K^{-1} mol^{-1} for amorphous SiO_2 and As_2O_3 by substituting the corresponding crystalline data $S°_{298}(SiO_2,c)$ = 41.84[15] or 41.46[21] J K^{-1} mol^{-1} and $S°_{298}(As_2O_3,c)$ = 107.1 J K^{-1} mol^{-1},[17] in eq 18 leads to the results cited in column 6 of Table 8. Here, the predicted values for of $S°_{298}(SiO_2,a)$ = 51.9 and 51.5 J K^{-1} mol^{-1} are between 8 and 10%, different from the experimental values.[15,21] For As_2O_3, the result is only 4% different, with $S°_{298}(As_2O_3,c)$ being 122.7 J K^{-1} mol^{-1} compared to the experimental value of 127.6 J K^{-1} mol^{-1}.

More reliable results, in the former case, can be obtained by abandoning the entropy correlation and instead using eq 19, which permits the calculation of $S°_{298}$(a) from $\Delta_f H°$(a) and $\Delta_f G°$(a) data and the corresponding standard entropies of the elements comprising the material under study:

$$S°_{298}(a) = [[\Delta_f H°(a) - \Delta_f G°(a)]/T] + \Sigma S°_{298}(\text{element}) \quad (19)$$

Thus, using the example of SiO_2: $\Delta_f H°(SiO_2,a)$ = −903.49[15] J K^{-1} mol^{-1} and $\Delta_f G°(SiO_2,a)$ = −850.7[15] J K^{-1} mol^{-1} and also

$S°_{298}(\mathrm{Si,c}) = 18.83^{15}$ J K^{-1} mol^{-1} and $S°_{298}(\mathrm{O_2,g}) = 205.138^{15}$ J K^{-1} mol^{-1}, so that using eq 19

$$\begin{aligned} S°_{298}(\mathrm{SiO_2,a}) &= [[\Delta_f H°(\mathrm{SiO_2,a}) - \Delta_f G°(\mathrm{SiO_2,a})]/T] \\ &\quad + S°_{298}(\mathrm{Si,c}) + S°_{298}(\mathrm{O_2,g}) \\ &= [(-903.49) - (-850.7)/0.298] + 18.83 \\ &\quad + 205.138 \\ &= 46.8\ \mathrm{J\,K^{-1}mol^{-1}} \end{aligned} \tag{20}$$

Thus, the estimate made for $S°_{298}(\mathrm{SiO_2,a})$ is almost equal to the experimental value of ref 15.

5. THE A/C THERMODYNAMIC RULES OF THUMB

The equations developed in this paper offer a guideline for the estimation of missing amorphous data in cases where crystalline data are known and constitute "rules of thumb" in the form of the following:

(i) Standard enthalpies of formation of amorphous materials are *usually approximately 99.3% of the corresponding standard enthalpy of formation of the crystalline material adjusted then by the addition of 13 kJ mol^{-1}.*

(ii) Standard Gibbs energies of formation of amorphous materials are *usually approximately 98.8% of the corresponding standard enthalpy of formation of the crystalline material adjusted then by the addition of 1 kJ mol^{-1}.*

In the case of standard entropy, the scatter on the graph (Figure 3) makes the prediction of data for amorphous materials rather tenuous. Until such time as more data are assembled, the mere hint of a possible linear correlation is very tentative and cannot be elevated even to the status of "rule of thumb". All three "rules" may need to be refined if more data come to light.

The authors are cogently aware that, generally, when plotting two large and similar magnitudes having a small difference between them, one will inevitably obtain a linear format. However, the correlation coefficients of the plots made here for standard enthalpies of formation and for Gibbs energies of formation are so near to $R^2 = 1$ that genuine correlations can be claimed. The results offer a means of obtaining a "ball park" estimate of missing data in a largely unstudied area; herein lies the value of this work.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Data of enthalpy plots and plots of the difference functions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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