Predictive Thermodynamics for Condensed Phases

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Supplementary Information

Examples of the Application of VBT

*Note: Numeric equation numbers refer to equations in the main text.*

Examples are here provided to illustrate the use of ion additivity, the isomegethic rule[R1] and equation (12), and to show the versatility of VBT for tackling practical synthetic as well as pedagogical problems. All of them, in the absence of the VBT initiative, would be difficult to tackle quantitatively.

Use of VBT to probe the thermodynamic stability / instability of hypothetical materials

Dioxygen dioxygenyl, O_4

Consider the following question: *Just how thermodynamically unstable is the hypothetical solid allotrope of dioxygen, dioxygenyl superoxide, $O_2^+O_2^-$ relative to the stable (gaseous) form of oxygen?*

This is best considered from the standpoint of a thermochemical cycle:

for which:

$$\Delta H \approx U_{POT}\{O_2^+O_2^-\} + RT - \Delta_f H^o\{O_2^+,g\} - \Delta_f H^o\{O_2^-,g\} \qquad (S1)$$

and
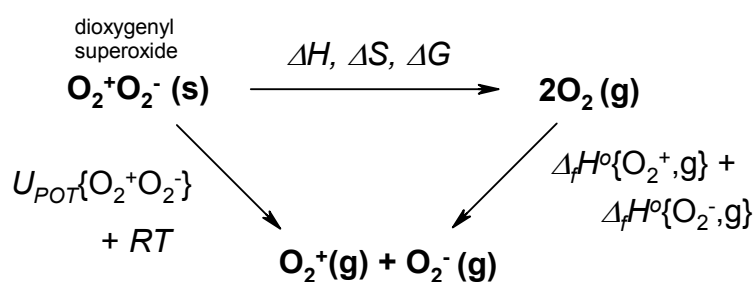
$$\Delta S \approx 2\, S^o_{298}\{O_2,g\} - S^o_{298}\{O_2^+O_2^-, s\} \qquad (S2)$$

and since, from standard tables:[R2] $\Delta_f H^o\{O_2^+,g\}$ / kJ mol^{-1} = 1170.9 (±0.9);

$\Delta_f H^o\{O_2^-,g\}$ / kJ mol^{-1} = -48.6 (±0.8) and $S^o_{298}\{O_2,g\}$ / J K^{-1} mol^{-1} = 205.147

(±0.005), then:

$$\Delta H \text{ / kJ mol}^{-1} \approx U_{POT}\{O_2^+O_2^-\} - 1119.8 \ (\pm 1.2) \qquad (S3)$$

and

$$\Delta S \text{ / J K}^{-1} \text{ mol}^{-1} \approx 410.3 - S^o_{298}\{O_2^+O_2^-, s\} \qquad (S4)$$

VBT thermodynamics can now provide the rest of the data required. From our

database:[R3] $V\{O_2^+\}/\text{nm}^3$ = 0.015 (±0.011); $V\{O_2^-\}/\text{nm}^3$ = 0.046 (±0.007) and hence

$V_m\{O_2^+O_2^-\}/\text{nm}^3$ = 0.061 (±0.013) for the 1:1 salt $O_2^+O_2^-$, for which $2I = \nu|z_+z_-| =$

2(1)(1) = 2 (equation (10)), hence $I = 1$, then (equation (12)): $U_{POT}\{O_2^+O_2^-\} = 2[\alpha$

$/V_m\{O_2^+O_2^-\}^{1/3} + \beta]$ where α = 117.3 kJ mol^{-1} nm and β = 51.9 kJ mol^{-1} leading to

$U_{POT}\{O_2^+O_2^-\}$ / kJ mol^{-1} $\approx$ 700 (±37) and hence to ΔH / kJ mol^{-1} $\approx$ -419.8 (±37).

$S^o_{298}\{O_2^+O_2^-, s\}$ / J K^{-1} mol^{-1} can be estimated from equation (6) and is approximated

by $1360\{V_m\{O_2^+O_2^-\} /\text{nm}^3\} + 15 = 1360 \{0.061 \ (\pm 0.013)\} + 15 = 98.0 \ (\pm 17.7)$ J K^{-1}

mol^{-1} and thus: ΔS / J K^{-1} mol^{-1} $\approx$ 312.3 (±17.7) J K^{-1}mol^{-1}, hence, at 298K, $T\Delta S \approx$

0.298{312.3 (±17.7) } = 93.1 (±5.3) kJ mol^{-1}. $\Delta G = \Delta H - T\Delta S$, and then $\Delta G \approx$ -419.8

(±37) - 93.1 (±5.2) $\approx$ - 512.9 (±37.4) kJ mol^{-1} indicating that *considerable*

thermodynamic instability is possessed by this solid oxygen allotrope, $O_2^+O_2^-$. This

arises both from the enthalpic difference between the solid and the gaseous forms and

the high entropy possessed by 2 moles of $O_2(g)$. It should be noted here that use of

Hofmann's elemental volumes[R4] (Table 2) leads to $V_m\{O_2^+O_2^-\}/\text{nm}^3$ = [4{11.39

(±0.17)] / 1000 = 0.0456 (±0.0003) which, although within the standard deviation

quoted above, is likely to be less reliable since Hofmann recommends taking account

of local environment when estimating volumes involving the atoms C, H, N, O and F.

Solid Ammonium Hydroxide, NH₄OH(s)

A similar exercise might be to use VBT to show why ammonium hydroxide does not

exist in the solid form and that the thermodynamic instability of this solid form of

$NH_4OH(s)$ is of the order of -135 kJ mol^{-1} with respect to $NH_3(g)$ and $H_2O(g)$.

$[V_m\{NH_4OH\} \approx 0.053\ (\pm 0.023)\ nm^3$; $I = 1$, $U_{POT}\{NH_4OH\} \approx 728\ (\pm 70)$ kJ mol^{-1}; ΔH

for the reaction: $NH_4OH(s) \rightarrow NH_3(g) + H_2O(g)$ is estimated to be $\approx$ -47.2 ($\pm$70.5) kJ

mol^{-1}; $S^o_{298}\{NH_4OH,s\} \approx 1360\ V_m\{NH_4OH\} + 15 \approx 87.1\ (\pm 31.2)$ J K^{-1} mol^{-1} leading

to ΔS / J K^{-1} mol^{-1} $\approx$ 294.5 ($\pm$31.2) kJ mol^{-1} and, hence, ΔG / kJ mol^{-1} $\approx$ -135.0

($\pm$71.1) kJ mol^{-1}].

Synthetic Problem: formation of LiSb₂F₁₁(s)

The reaction of LiF(s) and SbF₅(l) in 1:1 mole ratio is known to yield LiSbF₆(s): can

this be rationalized? Would doubling the mole ratio of SbF₅(l) be likely to

(thermodynamically) favour the formation of LiSb₂F₁₁(s)?

 The two reactions involved are:

$$LiF(s) + n\ SbF_5(l) \xrightarrow[\Delta G_n]{\Delta H_n,\ \Delta S_n} LiSb_nF_{5n+1}(s) \qquad (n = 1, 2) \qquad (S5)$$
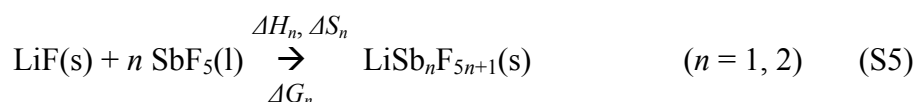
Consider first the case where $n = 1$:

ΔH_1 / kJ mol^{-1} = $\Delta_f H^o\{LiSbF_6,s\}$ - $\Delta_f H^o\{LiF,s\}$ - $\Delta_f H^o\{SbF_5,l\}$ 　　(S6)

Burgess, Peacock and Sherry[R5] have prepared LiSbF₆ and measured $\Delta_f H^o\{LiSbF_6,s\}$ =

-2 062 kJ mol^{-1}. Thus, ΔH_1 can be calculated (via eq.S6) to be -118 kJ mol^{-1} (since[R5]

$\Delta_f H^o\{SbF_5,l\}$ = -1 328 kJ mol^{-1} and $\Delta_f H^o\{LiF,s\}$ = -615.9 kJ mol^{-1}). Similarly, since

$S^o_{298}\{LiF,s\}$ = 35.6 J K^{-1} mol^{-1} and $S^o_{298}\{SbF_5,l\}$ = 265 J K^{-1} mol^{-1}, then:

ΔS_1 / J K^{-1} mol^{-1} = $S^o_{298}\{LiSbF_6,s\}$ - $S^o_{298}\{LiF,s\}$ - $S^o_{298}\{SbF_5,l\}$

　　　　　　　　 = 　$S^o_{298}\{LiSbF_6,s\}$ - 300.6 　　　　　(S7)

but we have no experimental measurement currently available for $S^o_{298}\{\text{LiSbF}_6,\text{s}\}$.

However, using VBT, we can provide an estimate of the latter, using equation (6),

provided we have data for $V_m\{\text{LiSbF}_6\}$. This volume can be obtained by at least two

routes (Figure 3). From crystal structure data,[R6] the hexagonal unit cell of LiSbF_6 has

lengths: $a = 0.518$ nm and $c = 1.360$ nm^3 with Z = 3, hence $V_m\{\text{LiSbF}_6\} = \sin(60°)$

$a^2c/\text{Z} = 0.1053$ nm^3 (using the formula in footnote (2) of ref. (R7)). Being

experimentally based, this is the preferred route by which to obtain $V_m\{\text{LiSbF}_6\}$; this

value can be checked (assuming additivity of single ion volumes) using our

database,[R3] whereby: $V_m\{\text{LiSbF}_6\} \approx V\{\text{Li}^+\} + V\{\text{SbF}_6^-\} \approx 0.123$ (±0.012) nm^3, just

larger than might have been expected.   Hence, using the experimental volume,

$S^o_{298}\{\text{LiSbF}_6,\text{s}\} \approx 158$ J K^{-1} mol^{-1}. Substitution into eq.(S7) then leads to $\Delta S_1 \approx -143$ J

K^{-1} mol^{-1} and, hence, to $\Delta G \approx -76$ kJ mol^{-1}, so confirming the experimental

observation that formation of LiSbF_6 is thermodynamically favoured in reaction (S5)

(with $n = 1$). Note also that, in adopting the VBT approach and in order to maximise

accuracy, *whenever possible* one should employ experimentally known data or data

from thermochemical tables, resorting to VBT procedures only in the absence of

information. While the difference between the two volumes in this case may be

regarded as substantial, its effect is considerably mitigated in use for enthalpy

calculations by the use of the cube-root of the formula unit volume.

In order to consider whether $\text{LiSb}_2\text{F}_{11}$ is thermodynamically likely to be the product

of reaction (S5) if n is doubled to 2, we can employ a cycle equivalent to that shown

in Figure 2 for this specific case. This leads to the equations:

ΔH_2 / kJ mol$^{-1} \approx \Delta_f H^o\{\text{Li}^+,\text{g}\} + \Delta_f H^o\{\text{Sb}_2\text{F}_{11}^-,\text{g}\} - \Delta_f H^o\{\text{LiF},\text{s}\}$

$$- \, 2 \, \Delta_f H^o\{\text{SbF}_5,\text{l}\} - U_{POT}\{\text{LiSb}_2\text{F}_{11}\} - \tfrac{1}{2}RT$$

$$\approx 440.4 \ (\pm 25) \ - U_{POT}\{LiSb_2F_{11}\}$$

(S8)

$$\Delta S_2 \ / \ \text{J K}^{-1} \ \text{mol}^{-1} \approx S^o_{298}\{LiSb_2F_{11},s\} - S^o_{298}\{LiF,s\} - 2 \ S^o_{298} \ \{SbF_5,l\}$$

$$\approx S^o_{298}\{LiSb_2F_{11},s\} - 565.7$$

(S9)

on substituting the known data above with $\Delta_f H^o\{Li^+,g\} = 685.78$ kJ mol^{-1}, and taking

$\Delta_f H^o\{Sb_2F_{11}^-,g\} \approx -3516 \ (\pm 25)$ kJ mol^{-1}, as determined from our recent *ab initio*

computations.[R8] The two remaining unknown pieces of data are $U_{POT}\{LiSb_2F_{11}\}$ and

$S^o_{298}\{LiSb_2F_{11},s\}$, both of which can be estimated via VBT, provided $V_m\{LiSb_2F_{11}\}$

can have been estimated (bearing in mind that we have no crystal structure data for

this hypothetical, as yet unsynthesized material).

However, we can use known crystal data, together with our isomegethic rule[R1] to

estimate the volume from known crystal structure data:

$$V_m\{LiSb_2F_{11}\} \approx 2V_m\{LiSbF_6\} + V_m\{LiF\}$$

(S10)

where $V_m\{LiF\} \ / \ \text{nm}^3 = 0.0163$ (LiF has cubic cell constants:[R6] $a = 0.40262$ nm, Z = 4

and, hence, $V_m\{LiF\} = a^3/Z$), while we already know $V_m\{LiSbF_6\}$ so that, from

equation (S10), $V_m\{LiSb_2F_{11}\} \ / \ \text{nm}^3 = \ 2(0.105) + 0.016 = 0.226$. From equations (12)

and (6) then $U_{POT}\{LiSb_2F_{11}\} \approx \ 489$ kJ mol^{-1} and $S^o_{298}\{LiSb_2F_{11},s\} \approx 322$ J K^{-1} mol^{-1}.

From equations (S8) and (S9): $\Delta H_2 \approx - \ 48.6 \ (\pm 25)$ kJ mol^{-1}; $\Delta S_2 \approx -244$ J K^{-1} mol^{-1} and

hence: $\Delta G_2 \approx + \ 24 \ (\pm 25)$ kJ mol^{-1}. We therefore conclude that preparation of LiSb$_2$F$_{11}$

is *very probably* thermodynamically unfavourable by route (S5) ($n = 2$), as is

(currently) consistent with experimental fact.

Use of VBT to probe quantitative thermodynamics of reactions involving gas /

liquid phase ions

Fluoride Ion affinity estimation The fluoride ion affinity, $FIA\{SbF_5,l\}$, of liquid

SbF_5 is represented by the enthalpy change of the reaction:

$$\Delta H = FIA\{SbF_5,l\}$$
$$F^-(g) + SbF_5(l) \quad \rightarrow \quad SbF_6^-(g) \tag{S11}$$
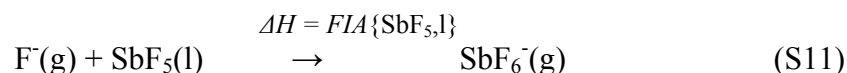
VBT can be used to obtain an estimate of this quantity (and of ΔH for similar

reactions involving gas phase ions). Firstly we note that adding a gaseous metal

cation, $M^+(g)$ to *both sides* of the reaction *does not change* the overall thermodynamic

enthalpy change, $\Delta H,$ of the reaction, thus:

$$\Delta H = FIA\{SbF_5,l\}$$
$$M^+(g) + F^-(g) + SbF_5(l) \quad \rightarrow \quad M^+(g) + SbF_6^-(g) \tag{S12}$$
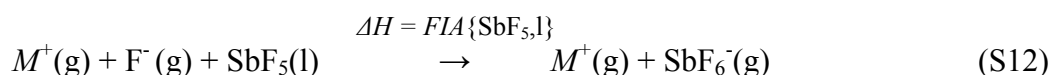
This addition then facilitates: (i) the construction of a thermochemical cycle based
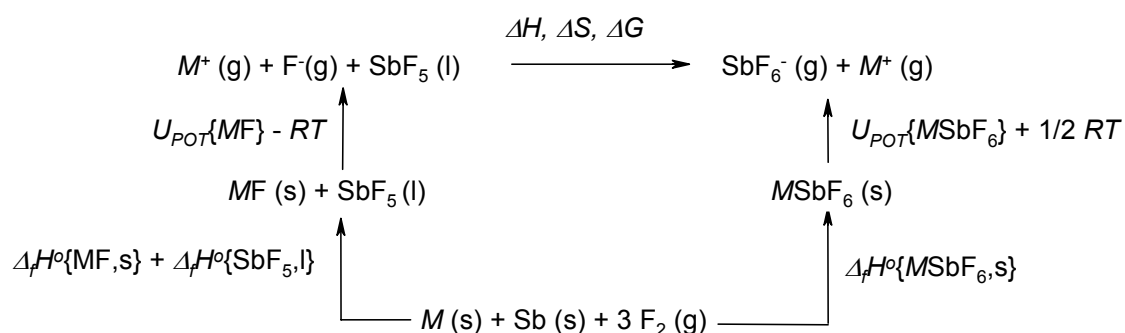
on the target reaction and (ii) the introduction of a (quantifiable) lattice potential

energy (enthalpy)[R9] step - which can be evaluated from tabulated data (in the case of

MF) or else can be estimated from VBT theory (in the case of MSbF$_6$). Provided then

that the standard enthalpies of formation of the artificially introduced salts,

$\Delta_f H^o\{M\text{F},s\}$ and $\Delta_f H^o\{M\text{SbF}_6,s\}$ are known then these can be combined with

$\Delta_f H^o\{SbF_5,l\} = -1\,328$ kJ mol^{-1} to obtain an estimate of $\Delta H\,(= FIA\{SbF_5,l\})$. The

process can be repeated for differing metal ions, M^+, provided data is available, and

then an average can be taken. We illustrate the calculation for $M^+ = K^+$. From the

cycle:

$$\Delta H \ (= FIA\{SbF_5, l\}) \ = U_{POT}\{MSbF_6\} - U_{POT}\{MF\} + 3/2 \ RT \ + \Delta_f H^o\{MSbF_6, s\}$$

$$- \Delta_f H^o\{MF, s\} - \Delta_f H^o\{SbF_5, l\} \qquad (S13)$$

for the potassium salts involved: $U_{POT}\{KF\}$ / kJ mol^{-1} = 808;[R10] $\Delta_f H^o\{KSbF_6, s\}$ / kJ

mol^{-1} = -2092;[R11] -2086,[R5] averaging to -2089 ($\pm$3); $\Delta_f H^o\{KF, s\}$ / kJ mol^{-1} = -567.3

and hence:

$$\Delta H \ (= FIA\{SbF_5, g\}) \ / \ kJ \ mol^{-1} = U_{POT}\{MSbF_6\} - 997.95 \ (\pm 3) \qquad (S14)$$

There are two crystal structure determinations for KSbF$_6$: the first[R12] reports a cubic

arrangement with a = 1.014 nm, Z = 8 and thus $V_m\{KSbF_6\}$ / nm^3 = a^3/8 = 0.1303

leading to a lattice energy (1:1 values of α and β, I = 1), $U_{POT}\{KSbF_6\}$ / kJ mol^{-1} =

567 and the second[R13] reports a tetragonal arrangement with: a = 0.516 nm, c = 1.007;

Z = 2 so that $V_m\{KSbF_6\}$ / nm^3 = a^{2}c/2 = 0.1341. The two crystal structure volumes

average to give: $V_m\{KSbF_6\}$ / nm^3 = 0.1322 ($\pm$0.019) leading to a lattice energy (1:1

values of α and β, I = 1), $U_{POT}\{KSbF_6\}$ / kJ mol^{-1} = 564. $\Delta H \ (= FIA\{SbF_5, l\})$ / kJ

mol^{-1} (from eq.(S14)) $\approx$ - 436 (equivalent to a pF$^-$ value [defined by the relationship:

pF$^-$(SbF$_5$,l) = (-FIA (SbF$_5$,l) / kcal mol^{-1}) / 10] = 10.4). This value is within the error

limits, although is somewhat higher than the value $FIA\{SbF_5, l\}$) / kJ mol^{-1} $\approx$ -475

($\pm$63) (equivalent to a pF$^-$ value = 11.4) which is obtained from a consideration of a

larger number of salts[R14] (i.e., varying M$^+$) in an identical fashion.

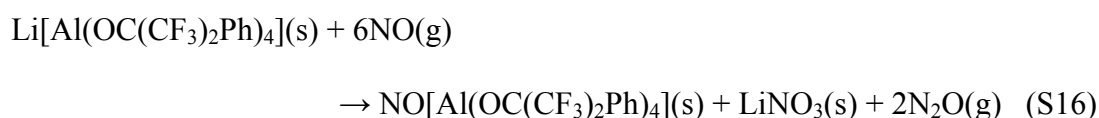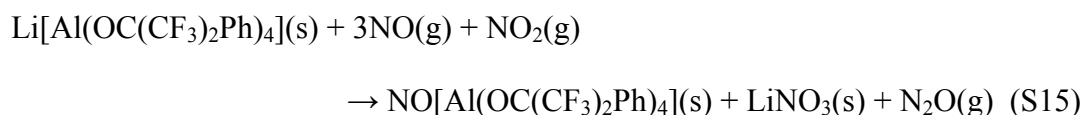A similar calculation could also be performed for SbF$_5$ *in the gaseous state* to give an

estimate for $FIA\{SbF_5, g\}$.

Use of VBT to probe the thermodynamics of complex solid / gas reactions
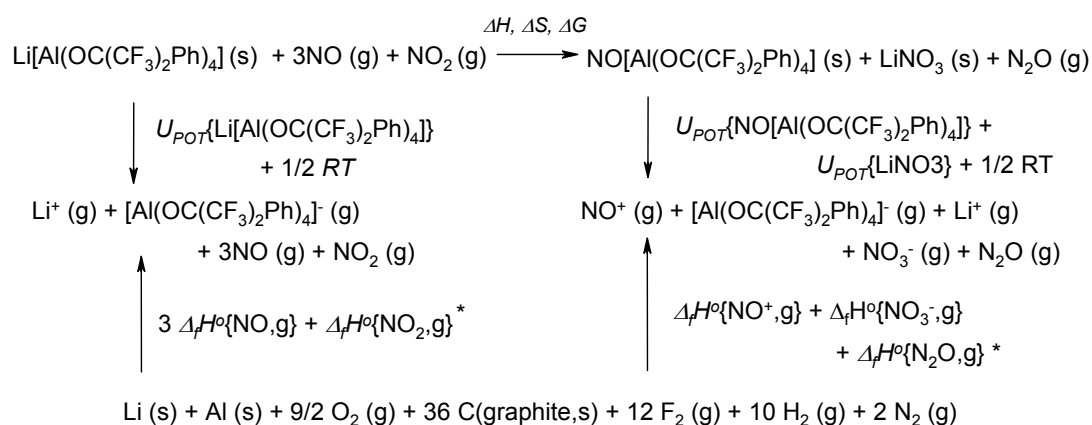
The NO/NO$_2$ – LiAl(OR)$_4$ reaction In the next example we use the VBT procedure

to investigate two alternative preparative routes for the salt NO[Al(OC(CF$_3$)$_2$Ph)$_4$]

using the solid-state reaction of Li[Al(OC(CF$_3$)$_2$Ph)$_4$] either with nitrogen oxides, NO

and NO_2 (i.e., by reaction (S15)) or exclusively with NO alone (i.e., by reaction

(S16)). Suppose we wish to decide which of the two following reactions is the more

thermodynamically favourable:

$Li[Al(OC(CF_3)_2Ph)_4](s) + 3NO(g) + NO_2(g)$

$$\rightarrow NO[Al(OC(CF_3)_2Ph)_4](s) + LiNO_3(s) + N_2O(g) \quad (S15)$$

$Li[Al(OC(CF_3)_2Ph)_4](s) + 6NO(g)$

$$\rightarrow NO[Al(OC(CF_3)_2Ph)_4](s) + LiNO_3(s) + 2N_2O(g) \quad (S16)$$

A suitable cycle by which to probe reaction (S15) is shown below:

$$\Delta H, \Delta S, \Delta G$$

$Li[Al(OC(CF_3)_2Ph)_4](s) + 3NO(g) + NO_2(g) \longrightarrow NO[Al(OC(CF_3)_2Ph)_4](s) + LiNO_3(s) + N_2O(g)$

$$\downarrow \quad U_{POT}\{Li[Al(OC(CF_3)_2Ph)_4]\} + 1/2\,RT \qquad\qquad \downarrow \quad U_{POT}\{NO[Al(OC(CF_3)_2Ph)_4]\} + U_{POT}\{LiNO3\} + 1/2\,RT$$

$Li^+(g) + [Al(OC(CF_3)_2Ph)_4]^-(g) \qquad\qquad NO^+(g) + [Al(OC(CF_3)_2Ph)_4]^-(g) + Li^+(g)$

$+ 3NO(g) + NO_2(g) \qquad\qquad\qquad + NO_3^-(g) + N_2O(g)$

$\uparrow \quad 3\,\Delta_f H^o\{NO,g\} + \Delta_f H^o\{NO_2,g\}^* \qquad\qquad \uparrow \quad \Delta_f H^o\{NO^+,g\} + \Delta_f H^o\{NO_3^-,g\} + \Delta_f H^o\{N_2O,g\}^*$

$Li(s) + Al(s) + 9/2\,O_2(g) + 36\,C(graphite,s) + 12\,F_2(g) + 10\,H_2(g) + 2\,N_2(g)$

* Enthalpies of formation which cancel out are omitted

for which:

$\Delta H = U_{POT}\{Li[Al(OC(CF_3)_2Ph)_4]\} - U_{POT}\{NO[Al(OC(CF_3)_2Ph)_4]\} - U_{POT}\{LiNO_3\}$

$$- 3\,\Delta_f H^o\{NO,g\} - \Delta_f H^o\{NO_2,g\} + \Delta_f H^o\{NO^+,g\}$$

$$+ \Delta_f H^o\{NO_3^-,g\} + \Delta_f H^o\{N_2O,g\} \qquad (S17)$$

$\Delta S = S^0{}_{298}\{NO[Al(OC(CF_3)_2Ph)_4],s\} - S^0{}_{298}\{Li[Al(OC(CF_3)_2Ph)_4],s\}$

$$+ S^0{}_{298}\{LiNO_3,s\} + S^0{}_{298}\{N_2O,g\} - 3\,S^o{}_{298}\{NO,g\} - S^o{}_{298}\{NO_2,g\} \quad (S18)$$

Substitution of known thermodynamic data into equations (S17) and (S18) leads to

the following:

ΔH / kJ mol^{-1}

$$= U_{POT}\{Li[Al(OC(CF_3)_2Ph)_4]\} - U_{POT}\{NO[Al(OC(CF_3)_2Ph)_4]\} - U_{POT}\{LiNO_3\}$$

$$- 3\,\{90.29\} - \{33.10\} + \{990.3\} + \{-306\,(\pm1.3)\} + \{82.05\}$$

$$= U_{POT}\{Li[Al(OC(CF_3)_2Ph)_4]\} - U_{POT}\{NO[Al(OC(CF_3)_2Ph)_4]\}$$

$$- U_{POT}\{LiNO_3\} + 462.4\,(\pm1.3) \qquad (S19)$$

and

$$\Delta S \,/\, J\,K^{-1}\,mol^{-1} = S^0_{298}\{NO[Al(OC(CF_3)_2Ph)_4],s\} - S^0_{298}\{Li[Al(OC(CF_3)_2Ph)_4],s\}$$

$$+ \{90.9\} + \{219.96\} - 3\,\{210.76\} - \{240.40\}$$

$$= S^0_{298}\{NO[Al(OC(CF_3)_2Ph)_4],s\} - S^0_{298}\{Li[Al(OC(CF_3)_2Ph)_4],s\}$$

$$- 561.8 \qquad (S20)$$

To apply VBT we now need $V_m\{NO[Al(OC(CF_3)_2Ph)_4]\}$ and

$V_m\{Li[Al(OC(CF_3)_2Ph)_4]\}$. Since we have the latter material as a starting compound,

we could perform a crystal structure determination to provide its formula unit volume.

Instead we resort to employing Hofmann's elemental volumes,[R4] whereupon:

$V_m\{NO[Al(OC(CF_3)_2Ph)_4]\} \,/\, nm^3$

$$\approx [11.8\,(\pm1.3) + 5\{11.39\,(\pm0.17)\} + 39.6\,(\pm1.3) + 36\{13.87\,(\pm0.05)\}$$

$$+ 24\{11.17\,(\pm0.15)\} + 20\{5.08\,(\pm0.04)\}] \,/\, 1000$$

$$\approx 0.977\,(\pm0.004) \qquad (S21)$$

and $V_m\{Li[Al(OC(CF_3)_2Ph)_4]\}$ can then be found by the (exchange) relationship:

$V_m\{Li[Al(OC(CF_3)_2Ph)_4]\} \,/\, nm^3$

$$\approx V_m\{NO[Al(OC(CF_3)_2Ph)_4]\} - V\{NO^+\} + V\{Li^+\}$$

$$\approx [977\,(\pm4) - \{11.8\,(\pm1.3) + 11.39\,(\pm0.17)\} + 22.6\,(\pm0.9)] \,/\, 1000$$

$$\approx 0.976\,(\pm0.019) \qquad (S22)$$

Employing the values[R14]: $V\{NO^+\}\,/\, nm^3 = 0.010\,(\pm0.010)$ and $V\{Li^+\} \,/\, nm^3 = 0.002$:

$V_m\{Li[Al(OC(CF_3)_2Ph)_4]\} \,/\, nm^3$

$$\approx [0.977\,(\pm0.004) - 0.010\,(\pm0.010) + 0.002]$$

$$\approx 0.969 \ (\pm 0.010) \qquad\qquad (S23)$$

leading to: $U_{POT}\{NO[Al(OC(CF_3)_2Ph)_4]\}$ / kJ mol^{-1} $\approx$ 340   and

$U_{POT}\{Li[Al(OC(CF_3)_2Ph)_4]\}$ / kJ mol^{-1} $\approx$ 341 (note the similarity of lattice energies

for the nitroso and the lithium salts - arising because the anion $[Al(OC(CF_3)_2Ph)_4]^-$ is

so very large when compared to the cations).

It is worthwhile noting that once the product, $NO[Al(OC(CF_3)_2Ph)_4])$, was

acquired,[R15] a crystal structure determination showed its volume to be 0.9825 nm^3,

this value is within 0.006 nm^3 of our estimated value.

$U_{POT}\{LiNO_3\}$ can be obtained from crystal structure data (hexagonal: a = 0.4693 nm, c =

1.5224 nm, Z = 6 so that $V_m\{LiNO_3\} = a^2c \sin 60^o / Z = 0.048$ nm^3 leading (by eq.12) to

$U_{POT}\{LiNO_3\}$/ kJ mol^{-1} = 749) or from experimental density (eq.7), ρ / g cm^{-3} = 2.366

and M = 68.946 g mol^{-1}, leading, similarly, to $V_m\{LiNO_3\}$ = 0.048 nm^3. A study of the

nitrate lattice energies based on viscosity data[R16] gave rise to the value: $U_{POT}\{LiNO_3\}$ / kJ

mol^{-1} = 848. The estimated value of $U_{POT}\{LiNO_3\}$ (eq. 12) is 748 kJ mol^{-1}, using the

preferred experimentally-derived volume.

The difference in entropy:

$[S^0{}_{298}\{NO[Al(OC(CF_3)_2Ph)_4],s\} - S^0{}_{298}\{Li[Al(OC(CF_3)_2Ph)_4],s\}]$

can be approximated, simply, by $[k \ (V\{NO^+\} - V\{Li^+\})]$ adopting the assumption of ion

additivity in conjunction with equation (6), so that, since k = 1360 J K^{-1} mol^{-1} nm^{-3} and

taking ion volumes from our database:[R14] $V\{NO^+\}$/ nm^3 = 0.010 ($\pm$0.010) and $V\{Li^+\}$ /

nm^3 = 0.002 so that the difference in entropy is 10.9 ($\pm$13.6) J K^{-1} mol^{-1}.

Using the above estimates from VBT leads to the values: $\Delta H \approx$ -286 kJ mol^{-1} (eq.

S19) and $\Delta S \approx$ -550.9 ($\pm$13.6) J K^{-1} mol^{-1} (eq. S20), so that (at 298K) ΔG for reaction

(S15) is estimated to be -122 ($\pm$14) kJ mol^{-1}.

Consideration of the second reaction (S16) will lead to the following equations:

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$$\Delta H = U_{POT}\{Li[Al(OC(CF_3)_2Ph)_4]\} - U_{POT}\{NO[Al(OC(CF_3)_2Ph)_4]\} - U_{POT}\{LiNO_3\}$$

$$- 6\ \Delta_fH^o\{NO,g\} + \Delta_fH^o\{NO^+,g\} + \Delta_fH^o\{NO_3^-,g\} + 2\ \Delta_fH^o\{N_2O,g\} \qquad (S23)$$

$$\Delta S = S^0{}_{298}\{NO[Al(OC(CF_3)_2Ph)_4],s\} - S^0{}_{298}\{Li[Al(OC(CF_3)_2Ph)_4],s\}$$

$$+ S^0{}_{298}\{LiNO_3,s\} + 2\ S^0{}_{298}\{N_2O,g\} - 6\ S^o{}_{298}\{NO,g\} \qquad (S24)$$

and using identical data to that discussed above, to $\Delta H \approx$ -440 kJ mol^{-1}; ΔS

$\approx$ -722.8 ($\pm$13.6) J K^{-1} mol^{-1}, so that (at 298K), ΔG for reaction (S16) is estimated to

be -225 ($\pm$14) kJ mol^{-1}.

The following conclusions can be made. Both reactions (S15) and (S16) are

thermodynamically favourable - the latter more than the former by some 100 kJ mol^{-1}

and both are enthalpically driven. The formation of the $LiNO_3$ structure, in the course

of these reactions, features as an important enthalpic driving force, whilst the

disruption and formation of the $Li[Al(OC(CF_3)_2Ph)_4]$ and $NO[Al(OC(CF_3)_2Ph)_4]$

respectively, which takes place during both reactions, hardly influences the overall

energetics.

Caveat

In attempting to apply these methods, it should always be remembered that VBT

offers us only a *rough guide* to the underlying thermodynamics but, in cases where

data is unknown, as in the above example, it serves to provide a *quantitative* estimate

of the likely situation (but does ignore kinetic factors).

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