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January 26, 1956

Date: 2/4/59
MEMORANDUM

FROM: E. A. POHL

THERMODYNAMIC VALUES OF INTEREST IN METALLURGY

Attached are several tables of free energy and heat of formation for the metals often encountered in metallurgy. They have been collated mainly from the NBS Circular #500, and are on a self-consistent basis. Table I gives a bird's eye view of the relative combining affinity of the elements, usually in pure solid or pure liquid states. As can be seen, the ability of one metal to replace another depends markedly upon the conditions. The order is different for fluorides, chlorides, oxides, sulfides, or in dilute aqueous solution. The latter order is the familiar "electromotive series", Table VI.

The values of the free energy or heat of reaction as given in Tables I through V are for the metals and their salts in the "standard state"--i.e. with unit activity such as for pure metal or salt. Care must be exercised in their use. The effects of dilution are in the direction as to oppose an expected reaction's completion. For example, according to the table of free energies in the standard states (or what is numerically nearly the same for most cases, the heats of reaction) as shown in Table I, one would expect uranium to reduce aluminum oxide by the reaction:

where the symbol (c) indicates the crystal or "standard" state. However, uranium dissolves in aluminum and checks the completion of the reaction. A similar argument applies, for example, to the reduction of PuO_2 by Ca. This entropy effect becomes especially large at high dilution and at elevated temperatures. It is shown in figures VII and VIII that the dilution effect in this case is comparable to the "standard" free energy difference at concentrations of 5 mol percent or less at temperatures above $800^\circ K$. Accordingly, it generally is best to regard the standard free energy values only as rough guides as to whether or not a reaction can "go". The effects of dilution and temperature upon the extent of reaction are large, and must usually be considered.

MASTER

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The effects of dilution were calculated assuming that the solution of U in Al were "perfect", i.e. that $\Delta H = 0$. The calculation follows:

S = entropy per mol

F = free energy per mol

H = heat of reaction per mol

T = absolute temperature

R = gas constant

x_i = mol fraction of i th component.

(1) Since $\Delta F = \Delta H - T\Delta S$

and in perfect solutions

(2) $\Delta H = 0$, then

$$(\Delta F)_T = -T\Delta S$$

$$= RT \sum x_i \ln x_i$$

by definition
(cf. Dodge, Eq. IV-52)

in 5% U in Al

$$x_u = \frac{W_u/M_u}{W_u/M_u + W_{Al}/M_{Al}}$$

where W_i = weight of i th component

M_i = atomic weight of i th component

$$x_u = \frac{\frac{.05}{238}}{\frac{.05}{238} + \frac{.95}{27}} = .006008$$

$$x_{Al} = 1 - x_u = .993992$$

$$\begin{aligned} (\Delta F)_T &= (.993992 \ln .993992 + .006008 \ln .006008) RT \\ &= -.03682 RT \end{aligned}$$

at $T = 1300^\circ K$

$$\Delta F_{1300} = -.03682 \times 1.986 \times 1300 = -95.06 \text{ cal/mol solution}$$

$$\Delta F'_{1300} = \frac{-95.06}{.006008} = -15,820 \text{ cal/mol U in solution}$$

In a similar manner calculations were made for several selected temperatures and compositions.

Figure IA shows the free energy excess required to drive a reaction to the indicated level of completion if one reactant is in dilute solution.

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FIGURE 1A

Free Energy Excess Required To
Reduce Concentration of Dissolved
Reactant (e.g. oxide in metal) to level shown.

TABLE I

Heats of Formation @ 298.16°K, Energy per Average Bond
Data from NBS Circ. 500.

Element	Oxide $-\Delta H^\circ_f$, Kcal/mol	Fluoride $-\Delta H^\circ_f$, Kcal/mol	Chloride $-\Delta H^\circ_f$, Kcal/mol	Sulfide $-\Delta H^\circ_f$, Kcal/mol
Y ⁺⁺⁺	79 (from Ephraim)		78.3	
La ⁺⁺⁺	76.3		87.9	51.1
Ca ⁺⁺	75.95	145.2	95.0	57.7
Pr ⁺⁺⁺	74.1		85.9	
Nd ⁺⁺⁺	73.7		84.8	46.97
Sc ⁺⁺⁺			73.6	
Be ⁺⁺	73.0	125.7	61.2	28.0
Th ⁺⁺⁺⁺	73.0	119.3	71.2	43.7 (Th ₂ S ₃)
Mg ⁺⁺	71.92	131.8	76.7	41.5
Li ⁺	71.2	146.3	97.70	
Sr ⁺⁺	70.55	145.2	99.0	54.1
Pu ⁺⁺	68 ± 3	----	----	---
Pu ⁺⁺⁺		124.9 (PuF ₃ ,aq.)	76.7	
Np ⁺⁺⁺		120	73	
U ⁺⁺⁺		119	71	
U ⁺⁺⁺⁺	67.5	110.8	62.8	
Ba ⁺⁺	66.7	143.5	102.78	53.0
Al ⁺⁺⁺	66.52	103.7	55.4	20.27
Pu ⁺⁺⁺⁺	62.8	124.9	76.7	
Ce ⁺⁺⁺			86.8	49.8
Ce ⁺⁺⁺⁺	58.3			
Si ⁺⁺⁺⁺	51.4	92.5 (SiF ₄ gas)	38.3 [SiCl ₄ (liq)]	17.4
Na ⁺	49.7	136.0	97.755	44.6
K ⁺	43.2	134.46	104.175	50.0
Fe ⁺⁺	31.9		40.8	11.36
C ⁺⁺	13.208 (CO,gas)	40.8 (CF ₄ ,gas)	8.3 (CCl ₄ , liq)	-10.5 (CS ₂ liq)

TABLE II
Fluorides

<u>Compound</u>	<u>ΔH°_f</u>	<u>$\Delta H^\circ_f/F$</u>	<u>ΔF°_f</u>	<u>$\Delta F^\circ_f/F$</u>
LiF (c)	-146.3	-146.3	-139.6	-139.6
CaF ₂ (c)	-290.3	-145.2	-277.7	-138.9
SrF ₂ (c)	-290.3	-145.2		
BaF ₂ (c)	-286.9	-143.5	-274.5	-137.3
NaF (c)	-136.0	-136.0	-129.3	-129.3
KF (c)	-134.46	-134.46	-127.42	-127.42
MgF ₂ (c)	-263.5	-131.8	-250.8	-125.4
BeF ₂ (aq)	-251.4	-125.7		
PuF ₃ (aq)	-374.6	-124.9		
NpF ₃ (c)	-360.	-120.		
ThF ₄ (c)	-477.	-119.3		
UF ₃ (c)	-357.	-119.	-339.	-113.
UF ₄ (c)	-443.	-110.8	-421.	-105.3
AlF ₃ (c)	-311.	-103.7	-294.	- 98.
SiF ₄ (g)	-370.	- 92.5	-360.	- 90.
CF ₄ (g)	-162.5	- 40.8	-151.8	- 37.95
FeF ₂ (aq)	-177.8	- 88.9		

TABLE IIIChlorides

<u>Compound</u>	<u>ΔH°_f</u>	<u>$\Delta H^\circ_f/\text{Cl}$</u>	<u>ΔF°_f</u>	<u>$\Delta F^\circ_f/\text{Cl}$</u>
K Cl (c)	-104.175	-104.175	- 97.592	-97.592
BaCl ₂ (c)	-205.56	-102.78	-193.8	-96.9
SrCl ₂ (c)	-198.0	- 99.0	-186.7	-93.4
NaCl (c)	- 97.755	- 97.755	- 98.232	-98.232
LiCl	- 97.70	- 97.70		
CaCl ₂ (c)	-190.0	- 95.0	-179.3	-89.7
LaCl ₃ (c)	-263.6	- 87.9		
CeCl ₃ (α)	-260.3	- 86.8		
PrCl ₃ (c, α)	-257.8	- 85.9		
NdCl ₃ (α, c)	-254.3	- 84.8		
TaCl ₃ (c)	-234.8	- 78.3		
PuCl ₃ (c)	-230.0	- 76.7		
MeCl ₂ (c)	-153.4	- 76.7	-141.57	-70.8
ScCl ₃	-220.8	- 73.6		
NpCl ₃ (c)	-216.	- 73.		
ThCl ₄ (c)	-285.	- 71.2		
U Cl ₃ (c)	-213.	- 71.	-196.9	-65.6
U Cl ₄ (c)	-251.2	- 62.8	-230.0	-57.5
BeCl ₂ (c)	-122.3	- 61.2		
AlCl ₃	-166.2	- 55.4	-152.2	-50.73
FeCl ₂ (c)	- 81.5	- 40.8	- 72.2	-36.1
SiCl ₄ (l)	-153.0	- 36.3	-136.9	-34.2
C Cl ₄ (l)	- 33.3	- 8.3	- 16.4	- 4.1

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TABLE IV

Oxides

<u>Compound</u>	<u>ΔH°_f</u>	<u>$\Delta H^\circ_f/\text{bond}$</u>	<u>ΔF°_f</u>	<u>$\Delta F^\circ_f/\text{bond}$</u>
Y_2O_3 (c)	(774)	(Ephraim)		
La_2O_3 (c)	-458.	-76.3		
CaO (c)	-151.9	-75.95	-144.4	-72.2
Pr_2O_3 (c)	-444.5	-74.08		
Nd_2O_3 (c)	-442.0	-73.7		
BeO (c)	-146.0	-73.0	-139.0	-69.5
ThO_2 (c)	-292.	-73.0		
MgO (c)	-143.84	-71.92	-136.13	-68.6
Li_2O (c)	-142.4	-71.2		
SrO (c)	-141.1	-70.55	-133.8	-66.9
PuO	135 ± 6	68 ± 3	----	----
UO_2 (c)	-270.	-67.5	-257.	-64.3
BaO (c)	-133.4	-66.7	-126.3	-63.2
Al_2O_3 (c, α)	-399.09	-66.52	-376.77	-62.795
PuO_2 (c)	-251.	-62.8		
CeO_2 (c)	-233.	-58.3		
SiO_2 (c) quartz II	-205.4	-51.4	-192.4	-48.1
Na_2O (c)	- 99.4	-49.7		
K_2O (c)	- 86.4	-43.2		
$\text{Fe}_{0.95}\text{O}$	- 63.7	-31.9	- 58.4	-29.2
CO (g)	- 26.4157	-13.208	- 32.8079	-16.404

TABLE V
Sulfides

<u>Compound</u>	<u>ΔH°_f</u>	<u>$\Delta H^\circ_f/S$</u>	<u>ΔF°_f</u>	<u>$\Delta F^\circ_f/S$</u>
CaS (c)	-115.3	-57.7	-114.1	-57.1
SrS (c)	-108.1	54.1		
BaS (c)	-106.0	53.0		
La ₂ S ₃ (c)	-306.8	-51.1		
K ₂ S (c)	-100.	-50.		
Ce ₂ S ₃ (c)	-298.7	-49.8		
Nd ₂ S ₃ (c)	-281.8	-46.97		
Na ₂ S (c)	- 89.2	-44.6		
Th ₂ S ₃ (c)	-262.0	-43.7		
MgS (c)	- 83.0	-41.5		
BeS (c)	- 55.9	-27.95		
Al ₂ S ₃ (c)	-121.6	-20.27	-117.7	-19.6
SiS ₂ (c)	- 34.7	-17.4		
FeS (α)	- 22.72	-11.36	- 23.32	-11.66
CS ₂ (liq)	+ 21.0	+10.5	+ 15.2	+ 7.6

TABLE VI

Electromotive Series of the Elements

Li

Rb

K

Ba

Sr

Ca

Na

Mg

Be

$U^{+++} (\Delta F^{\circ}_f = -124.4)$

$U^{++++} (\Delta F^{\circ}_{faq} = -138.4)$

$Al^{+++} (\Delta F^{\circ}_{aq} = -115.0)$

Mn

Zn

Cr

Fe

Cd

Co

Ni

Sn

Pb

H

$\begin{pmatrix} Sb \\ As \\ Bi \end{pmatrix}$

Ag

Cu

Pd

Hg

Pt

Au

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