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A CATALYTIC PITCH GASIFICATION

PROCESS

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SYNTHETIC FUELS RESEARCH LABORATORY

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A Catalytic "pitch" gasification process?

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Summary

The question has been raised whether it would be of advantage to apply

catalysts in the gasification of Athabasca pitch derived from thermal hydro-

cracking of Athabasca tar.   More in particular it was asked which type of

catalyst would be optimal in this connection.

The problem was attacked from the knowledge that catalytic oxidation

reactions commonly operate as follows:

    a) the oxidic catalyst reacts with the feed by using part of the

       oxygen from its structure thereby becoming reduced

    b) it becomes oxidized again by interaction with O_2 or H_2O

Since both reactions should be as fast as possible neither of the two

should be strongly endothermic.   This was the basis of the method applied,

the problem being narrowed down by demanding that the reoxidation should be

performed by H_2O.   This introduces restraints posed by thermochemistry.   In

general, this restraint can be formulated as

$$\Delta H^O_f \ (Me_p \ O_{q+1}) - \Delta H^O_f \ (Me_p \ O_q) \ is \ ^{-50} \ to \ ^{-65} \ kcal \ Mol \ ^{-1}$$

when the heat of formation relate to the ozidized and the reduced form of

the catalyst (Me = metal) Pairs of compounds in this range are $MoO_3 \rightarrow MoO_2$,

$V_2O_4 \rightarrow V_2O_3$ and $Fe_2O_3 \rightarrow Fe_3O_4$ which therefore appear   feasible for

the gasification reaction.   One of these (V) is present in the feed.

1.   Introduction

    The CANMET Laboratories are considering the possibilities for the gas-

    ification of the residual pitch after distillation of the thermally

    hydrocracked Athabasca tar.   One of the sub problems to be considered

in this connection is the application of catalysts which in its turn
introduces the question of which catalyst to use.

It is the latter problem which will be considered here. The method
used is as follows:

It has been found in most catalytic oxidation reactions (although
not in all) that a good model for the mechanism is to assume that the
feed molecule is oxidized by the oxygen anions of the catalyst leading
to its reduction followed by its reoxidation by either O_2 or H_2O.
Therefore, when the catalyst in the highest oxidation state is written
as $Me_p O_{q+1}$ and in the lowest oxidation state as $Me_p O_q$ (Me being the
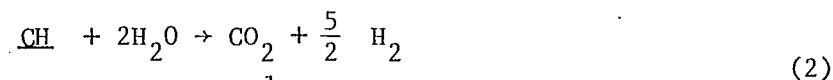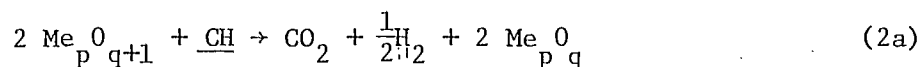metal) the model given is

a) $Me_p O_{q+1} + F \rightarrow Me_p O_q + P_1$

$$(1)$$

b) $Me_p O_q + 0\text{-donor} \rightarrow Me_p O_{q+1} + P_2$
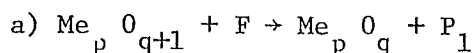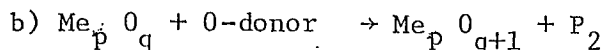
where F is feed molecule and P_1, P_2 are product molecules. The case that
will interest us particularly is that where the 0-donor is H_2O so that P_2
is H_2. Since the feed molecule is a hydrocarbon P_1 is either $CO_2 + H_2$,
$CO + H_2O$ or a mixture of both. It is more difficult to characterize the
feed for our special case. Athabasca residual pitch is a mixture of
polyaromatic molecules, presumably containing hydrogen in a ratio H/C is 1
while there is also a considerable amount of S present in the pitch
molecules. We shall consider three model compounds

1) F = graphite, an ultimate polyaromatic with no hydrogen

2) F = benzene, a monoaromatic with H/C = 1

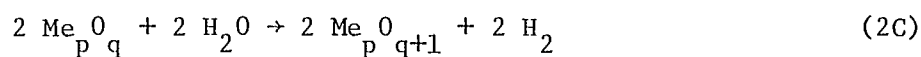3) F = thiophene, a heteroaromatic with H/C = 1 and one S -atom
   per molecule

Now let us consider a special instance, viz the oxidation of benzene
to $CO_2 + H_2$. We then get

$$\underline{CH} + 2H_2O \rightarrow CO_2 + \frac{5}{2} H_2 \tag{2}$$

(where $\underline{CH}$ stand for $\frac{1}{6} C_6H_6$

$$2 Me_p O_{q+1} + \underline{CH} \rightarrow CO_2 + \frac{1}{2}H_2 + 2 Me_p O_q \tag{2a}$$

and

$$2 Me_p O_q + 2 H_2O \rightarrow 2 Me_p O_{q+1} + 2 H_2 \tag{2C}$$

The first reaction is exothermic unless the heat of dissociation of
oxygen is so large that it surpasses the heat of formation of CO_2. On
the other hand, the second reaction is endothermic unless the heat of
dissociation is able to compensate for double the heat of formation of
H_2O.

Those two conditions pose constraints on the chice of the oxide.
If we call $\Delta H^o(0) = \Delta H^o_f (Me_p O_{q+1}) - \Delta H^o_f (Me_p O_q)$ then the heats of
formation of the two subreactions $\Delta H^o_r (a)$ and $\Delta H^o_r(b)$ are

$$\Delta H^o_r(a) \quad -97.35 - 2\Delta H^o(0) \tag{3a}$$

$$\Delta H^o_r(b) = 115.6 + 2\Delta H^o(0) \tag{3c}$$

The two straight lines will cross at a point where the heats of
reaction are each half the value of the overall heat (+18.25 kcal)
i.e. about 9 kcal endotherm at a value of $\Delta H^o(0)$ -53 kcal mol^{-1}
We consider this point as indicative for the most suitable catalyst.
Table I gives a list of $\Delta H^o(0)$ values for various pairs $Me_p O_{q+1} -$
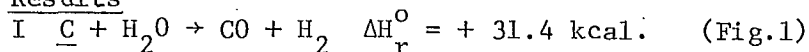$Me_p O_q$ and it is seen that the $Mo\ O_3 - Mo\ O_2$ fits very well i.e.
Starting from this criterion $Mo\ O_3$ should be promising as a potential

catalyst. Adopting a band width of $\pm$ 5 kcal mol^{-1} we find two other

candidates $Fe_2O_3 \rightarrow Fe_3O_4$ ($\Delta H^o(0) = -56$) and $V_2O_4 \rightarrow V_2O_3$ ($\Delta H^o(0) = -54$)

The latter has to be considered with some care because we do not know

whether V_2O_5 as a catalyst is actually present in a state intermediate

between V_2O_4 and V_2O_3 during the reaction but in first instance we shall

accept this as likely. Hence, catalysts in first instance worthy of

consideration are MoO_3, Fe_2O_3 and V_2O_5,

In the following similar computations will be made for the cases

I $\underline{C}$ (graphite) $+ H_2O \rightarrow CO + H_2$

II $\underline{CH}$ ($\frac{1}{6}C_6H_6$) $+ H_2O \rightarrow CO + 1.5\ H_2$

III $\underline{CH}$ ($\frac{1}{6}C_6H_6$) $+ 2H_2O \rightarrow CO_2 + \frac{5}{2} H_2$ (see above)

IV $\underline{CHS}_{1/4}$ ($\frac{1}{4}C_4H_4S$) $+ 2H_2O \rightarrow \frac{1}{4}H_2S + CO_2 + 2.25\ H_2$

V $\underline{CHS}_{1/4}$ $+ 2.5\ H_2O \rightarrow \frac{1}{4} SO_2 + CO_2 + 3H_2$

2. Results

I $\underline{C} + H_2O \rightarrow CO + H_2$ $\Delta H^o_r = + 31.4$ kcal.   (Fig.1)

     subreactions

a) $Me_pO_{q+1} + \underline{C} \rightarrow CO + Me_pO_q$

$$\Delta H_r (a) = -\Delta H^o(0) + \Delta H^o_f (CO)$$

$$= -\Delta H^o(0) - 26.4$$

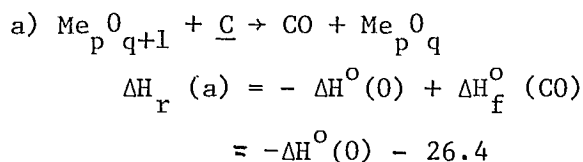b) $Me_pO_q + H_2O \rightarrow Me_pO_{q+1} + H_2$
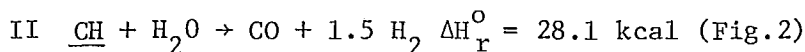
$$\Delta H_r(b) = \Delta H^o(0) + 57.8$$
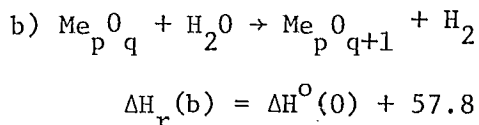
Fig. 1 shows that the intersection point is at $\Delta H^o(0) = -41.5$

As a consequence the two promising catalysts are

$Co_3O_4 \rightarrow 3\ CoO(-39)$ and $MoO_3 \rightarrow MoO_2$ (-50)

II $\underline{CH} + H_2O \rightarrow CO + 1.5\ H_2$ $\Delta H^o_r = 28.1$ kcal (Fig.2)

     subreactions

a) $1.5\ Me_pO_{q+1} + CH \rightarrow CO + 0.5\ H_2O + 1.5\ Me_pO_q$

$$\Delta H_r(a) = -1.5\ \Delta H^o(0) + \Delta H^o_f (CO) + 0.5\ \Delta H^o_f (H_2O)$$

$$- \Delta H^o_f (CH)$$

Taking ΔH_f^o (CH) $= \frac{1}{6} \Delta H_f^o$ $(C_6H_6) = + 3.3$

we find

$\Delta H_r(a) = - 1.5 \Delta H^o(0) - 58.6$

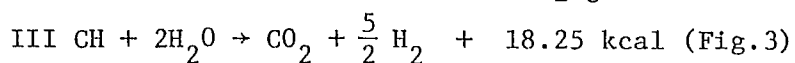b) $1.5 \text{ Me}_p O_q + 1.5 \text{ H}_2 O \to 1.5 \text{ Me}_p O_{q+1} + 1.5 \text{ H}_2$
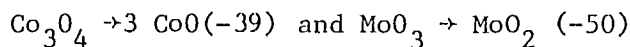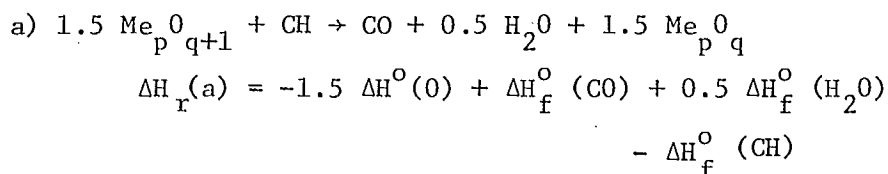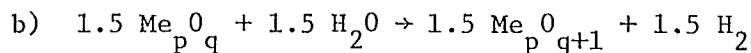
$\Delta H_r(b) = + 1.5 \Delta H^o(0) + 115.9$

The intersection point is at $\Delta H^o(0) = - 47.5$

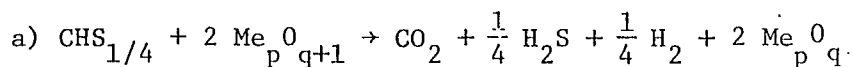Suitable catalysts are Co_3O_4 (-39), MoO_3(-50), V_2O_4(-54)

and Fe_2O_3 (-56)

III $CH + 2H_2O \to CO_2 + \frac{5}{2} H_2 + 18.25$ kcal (Fig.3)

given before

Catalysts MoO_3, V_2O_4 and Fe_2O_3

IV $CHS_{1/4} + 2 H_2O \to \frac{1}{4} H_2S + CO_2 + 2.25 H_2 + 12.5$ kcal (Fig.4)
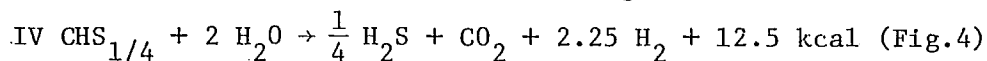
assumption ΔH_f^o $(C_4H_4S) = + 30.3$ kcal mol^{-1}

ΔH_f^o $(CHC_{1/4}) = + 7.6$ kcal mol^{-1}

subreactions

a) $CHS_{1/4} + 2 \text{ Me}_p O_{q+1} \to CO_2 + \frac{1}{4} H_2S + \frac{1}{4} H_2 + 2 \text{ Me}_p O_q$

$\Delta H_r^o(a) = - 103.15 - 2 \Delta H^o(0)$

b) $2 \text{ Me}_p O_q + 2H_2O \to 2 \text{ Me}_p O_{q+1} + 2H_2$

$\Delta H_r^o(b) = 115.6 + 2 \Delta H^o(0)$
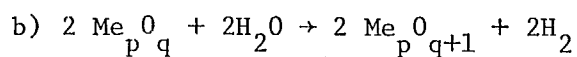
Intersection point - 54.5 kcal

Catalysts MoO_3, V_2O_4, Fe_2O_3

V $CHS_{1/4} + \frac{5}{2} H_2O \to \frac{1}{4} SO_2 + CO_2 + 3H_2 + 24.8$ kcal (Fig.5)

subreactions

a) $CHS_{1/4} + \frac{5}{2} \text{ Me}_p O_{q+1} \to \frac{1}{4} SO_2 + CO_2 + \frac{1}{2} H_2 + \frac{5}{2} \text{ Me}_p O_q$

ΔH_r^o (a) $= - 119.7 - \frac{5}{2} \Delta H_f^o$ (0)

b). $\frac{5}{2} Me_p O_q + \frac{5}{2} H_2 O \rightarrow \frac{5}{2} Me_p O_{q+1} + \frac{5}{2} H_2$

ΔH_r^o (b) $= 144.50 + \frac{5}{2} \Delta H_f^o$ (0)
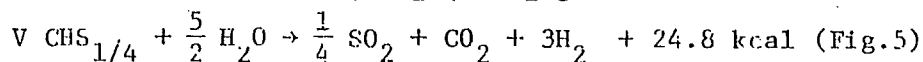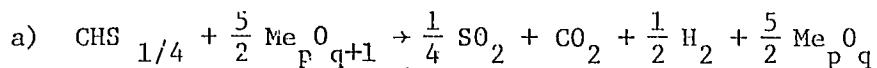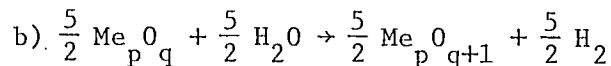
Intersection point ΔH_f^o (0) $= -52.5$

Catalysts MoO_3, V_2O_4, Fe_2O_3

Use of Standard free energies

The method followed so far is a rather crude simplification of Bahandin's principle ("Volcano curve" approximation). It would gain in credibility when applied for free energies instead of energies, the more so since entropical contributions are rather important because the reaction is accompanied by an increase in the number of molecules.

In order to estimate the potentialities of this approach two computations were made

I   For case III i.e. $CH + 2 H_2O \rightarrow CO_2 + \frac{5}{2} H_2$

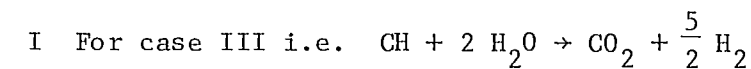II For the dehydrogenation of 1- butene to butadiene known to proceed over Fe_2O_3 - catalysts in the presence of steam at temperatures around $650^o C$.

The procedure followed was

1) calculate the free energy difference for the overall-reaction.

Results

I $CH + 2 H_2O \rightleftharpoons CO_2 + 5 H_2$

$\Delta G^o = 18250 - 18.10 \ T$

T for $\Delta G^o = o$ is $659^o K$ $(386^o C)$

II $C_4H_8 \rightarrow C_4H_6 + H_2$
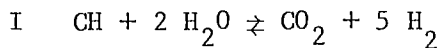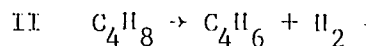
$\Delta G^o = 26470 - 24.45 \ T$

$T (\Delta G^o = o) = 1080^o K$ $(800^o C)$

2) Calculate free energy changes as done before for the heats

assuming

$$\Delta G^o(a) = \Delta G^o (b)$$

(Entropy differences for solids were neglected because these tend

to be small)

I $\Delta G^o(a) = - 126250 - \frac{5}{2} \Delta H^o(0) - 62.85\ T$

$\Delta G^o(b) = + 144500 + \frac{5}{2} \Delta H^o(0) + 34.75\ T$

gives

$\Delta H^o (0) = - 67\ kcal$

II $\Delta G^o (a) = 31050 - \Delta H^o (0) - 24.45\ T$

$\Delta G^o (b) = 57800 + \Delta H^o (0) + 13.90\ T$

gives

$\Delta H^o (0) = 65.2\ kcal$

The $\Delta H^o (0)$ values fall in the range for the reduction of Fe_2O_3

$$3Fe_2O_3 \rightarrow 2\ Fe_3O_4 \quad -56\ kcal$$

$$Fe_3O_4 \rightarrow 3FeO \quad -74\ kcal$$
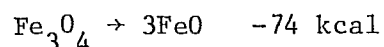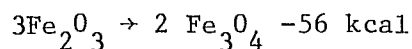
The result is found to justify the method used. From I we conclude

to Fe_2O_3 as a suitable catalyst, find that theoretically the results

should be very similar to those for the butene dehydogenation (where

actually Fe_2O_3 is used)

It is noteworthy that the temperatures at which the gasification

process can be applied   ($400^o C$) is much lower than that for the butene

dehydrogenation ($800^o C$)

The conclusion is that Fe_2O_3 appears very well suited to act as a

gasification catalyst. It might also be used as a scrubber for

S, SO_2, SO_3 to inhibit S-emission. Note that the use of free

energies instead of enthalpies tends to predict higher (more

negative) values of $\Delta H^o(0)$

3. Survey of literature data

   Apart from reports on potassium compounds supposed to act as

catalysts in coal gasification there is hardly any mention of

oxidation catalysts for gasification application. Indeed, for the

present case of a feed that is essentially liquid more information

might be found in the literature for the oxidation of compounds

such as naphtalene that are presumably more akin to the Athabasca

pitch. There are three industrial processes that might be envisaged

1) Oxidation of napthalene to phthalic anhydride catalyst $\underline{V_2O_5}$.

   Reaction condition, temperature around 400^oC, ratio air to

   naphtalene is 10. Operation either fixed bed or fluid bed. Only

   applicable if no side chains are present on the napthalene ring

   because these lead to complete combustion. (which for our object

   would be favourable)

2) Oxidation of benzene to maleic anhydride. Catalyst: $V_2O_5 + MoO_3$.

   Selectivity about 60%. Presence of side chains as in toluene

   leads to complete combustion. In actual operation (fixed bed) at

   temperatures around 400^oC the air/feed ratio is about stoichiometric

3) Oxidation of propene to acrolein. Catalyst for instance $Bi_2O_3 +$

   MoO_3. Temperature $400 - 500^oC$. Ratio of air/propene slightly

   higher than stoichiometric. Fixed bed. Steam might be used but is

   not effective in reoxidation of the catalyst.

4) Butene to butadiene. Old war-time process still in operation. One of the catalysts used was Fe_2O_3. Temperature is $650^O C$, <u>no</u> <u>oxygen</u>, <u>only</u> <u>steam</u> applied in excess. In absence of steam catalyst becomes reduced and inactive but can be reactivated by steam.

It is evident from this data that actual operation seems to follow the leads indicated before i.e. catalysts used are V_2O_5, MoO_3 and Fe_2O_3. The impression is gained that temperatures to be applied in the oxidation of pitch are around $600^O C$. A relevant observation is that side chains (probably present in the pitch) lead to complete combustion.

4. <u>Mixed oxygen donors</u> $(H_2O + O_2)$

So far the presence of O_2 in the feed was ignored mainly because it presents considerable difficulties in the method applied to search for an appropriate catalyst. Actually this method is only useful because it may be assumed that activation energies for endothermic reactions (as occurring in the case of H_2O as the oxygen donor) contain contributions of heats of reaction that often are considerable. With O_2 as the donor the reactions are exothermic and differences in reactivity originate from differences in activation energies not connected primarily with heats of reaction.

Let us consider case III for O_2 as the donor

$$CH + O_2 \rightarrow CO_2 + \frac{1}{2} H_2 \quad -94.35 \text{ kcal}$$
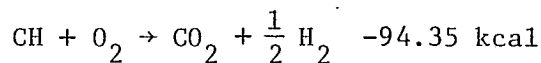
The reaction is strongly exothermic contrary to its equivalent for H_2O which is weakly endothermic (+18.25 kcal). The subreactions are

a) $2 \, Me_p O_{q+1} + CH \rightarrow CO_2 + \frac{1}{2} \dot{H}_2 + 2 \, Me_p O_q$
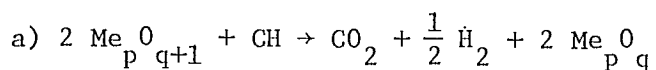
with

$\Delta H_r(a) = - 94.35 - 2\Delta H^O(0)$

similar to that of the steam reaction

b) $2Me_p O_q + O_2 \rightarrow 2 \, Me_p O_{q+1}$

$\Delta H_R(b) = + 2 \, \Delta \, H^O(0)$

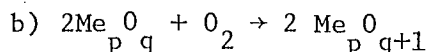This reaction is always exothermic contrary to the H_2O - analogue. (see broken line in fig.3). On the far left side the heat of reaction b is so low that incomplete oxidation might occur depending on the temperature. On the far right side the rate of oxidation of the hydrocarbon by the catalyst is too low because of it becoming strongly endothermic. So there is presumably a maximum in the rate as function of $\Delta H^O(0)$. It may be assumed that this maximum is situated to the left from that adopted for the steam reaction. Consequently the oxygen is rapidly consumed under heating up of the reaction volume, enabling the steam reaction to speed up provided that for both reactions a catalyst is present. Either therefore we operate with two catalysts (for instance $UO_3 + Mo \, O_3$ or $UO_3 + Fe_2O_3$) or we apply a catalyst that happens to show two reduction steps such as V_2O_5. It is interesting that the two steps for this compound viz. $V_2O_5 \rightarrow V_2O_4$ ($\Delta H^O(0) = -29$ and $V_2O_4 \rightarrow V_2O_3$ (-54) are approximately positioned at the critical points. The catalyst then can operate by adapting its oxygen content to the composition of the gas phase.

5. <u>Final remarks</u>

From what has been deduced in Section 2, it appears that sulfur in the feed might lead to the formation of SO_2 and perhaps SO_3. It is evident from the data that not much can be done to inhibit this reaction by a choice of catalyst. The only possibility to avoid the oxidation in trying to obtain the sulfur as H_2S or elemental sulfur is to adapt the steam pressure. This might be a serious difficulty since in actual operation the H_2O/O_2 ratio is already determined by other factors such as thermoneutrality.

Athabasca pitch contains considerable quantities of V and therefore might introduce its own catalyst. The ash in the pitch might act as a carrier and the final catalyst should contain 2 - 3% V on carrier which is - as experienced by this author - an acceptable catalyst provided the vanadium is on the surface of a non-porous support (such as SiC.)

TABLE I

$$\Delta H^o (0)$$

differences in heat of formation

of oxide-pairs

Pairs

Oxide - Oxide

Pairs $\Delta H^o (0)$ (kcal)

$3UO_3 \rightarrow U_3O_8$	-8	$V_2O_5 \rightarrow V_2O_4$	-29
$2\,Mn\,O_2 \rightarrow Mn_2O_3$	-17	$V_2O_4 \rightarrow V_2O_3$	-54
$Sb_2O_5 \rightarrow Sb_2O_4$	-20	$V_2O_3 \rightarrow V_2O_2$	-90
$V_2O_5 \rightarrow V_2O_4$	-29		
$1/2\ As_2O_5 - \frac{1}{2} As_2O_3$	-31	$2MnO_2 \rightarrow Mn_2O_3$	-17
$UO_3 \rightarrow UO_2$	-32	$MnO_2 \rightarrow MnO$	-32.5
$MnO_2 \rightarrow MnO$	-32.5	$Mn_2O_3 \rightarrow 2MnO$	-48
$2CuO \rightarrow Cu_2O$	-34	$Mn_3O_4 \rightarrow 3MnO$	-55
		$MnO \rightarrow Mn$	-92
$Co_3O_4 \rightarrow 3\,CoO$	-39		
$MoO_3 \rightarrow MoO_2$	-50	$3UO_3 \rightarrow U_3O_8$	-8
$V_2O_4 \rightarrow V_2O_3$	-54	$UO_3 \rightarrow UO_2$	-32
$3Fe_2O_3 \rightarrow 2Fe_3O_4$	-56		
$2WO_3 \rightarrow W_2O_5$	-64	$3Fe_2O_3 \rightarrow 2Fe_3O_4$	-56
		$Fe_3O_4 \rightarrow 3FeO$	-74
$WO_3 \rightarrow WO_2$	-65	$FeO \rightarrow Fe$	-64
$2TiO_2 \rightarrow Ti_2O_3$	-69	$2WO_3 \rightarrow W_2O_5$	-64
$SnO2 \rightarrow SnO$	-70	$WO_3 \rightarrow WO_2$	-65
$Fe_3O_4 \rightarrow 3FeO$	-74		
$Nb_2O_5 \rightarrow Nb_2O_4$	-74		

TABLE II

$\Delta H^o (0)$

differences in heat of formation of some oxides and their metals

Pairs	$\Delta H^o(0)$	Pairs	$\Delta H(0)$
$\frac{1}{3} Au_2O_3 \rightarrow 2/3\ Au$	+6.5	$1/3\ In_2O_3 \rightarrow 2/3\ In$	−74
$Ag_2O \rightarrow 2Ag$	−73	$MnO \rightarrow Mn$	−92
$\frac{1}{2} IrO_2 \rightarrow \frac{1}{2} Ir$	−20	$\frac{1}{3} Al_2O_3 \rightarrow 2/3\ Al$	−133
$PdO \rightarrow Pd$	−20	$\frac{1}{3} La_2O_3 \rightarrow \frac{2}{3} La$	−153
$RhO \rightarrow Rh$	−21.7		
$HgO \rightarrow Hg$	−21.7		
$1/2\ RuO_2 \rightarrow \frac{1}{2} Ru$	−26.3		
$1/2\ SiO_2 \rightarrow \frac{1}{2} Si$	−27.5		
$CuO \rightarrow Cu$	−37		
$1/2\ TeO_2 \rightarrow \frac{1}{2} Te$	−39		
$Tl_2O \rightarrow 2Tl$	−42		
$1/3\ Bi_2O \rightarrow 2/3\ Bi$	−46		
$PbO \rightarrow Pb$	−52		
$CoO \rightarrow Co$	−57		
$NiO \rightarrow Ni$	−58		
$FeO \rightarrow Fe$	−64		
$CdO \rightarrow Cd$	−61		
$\frac{1}{2} GeO_2 \rightarrow \frac{1}{2} Ge$	−64		

FIGURE 1

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H_r^O = 31.4 \, kcal$$

$$\Delta H_f^O(C) = \Delta H_f^O \, (GRAPHITE)$$

$$Co_3O_4 \rightarrow 3CoO$$

$$Mo_3 \rightarrow MoO_2$$

$$Me_pO_q + H_2O \rightarrow Me_pO_{q+1} + H_2$$

$$Me_pO_{q+1} + C \rightarrow CO + Me_pO_q$$

HEAT OF REACTION IN SUB-REACTION kcal

+80

+40

+20

0

−20

−40

10   30   50   70

$\Delta H^O(O)$ kcal

FIGURE 2

Plot of HEAT OF REACTION IN SUB-REACTION kcal (y-axis, from -40 to 80) versus $\Delta H^O(O)$ kcal (x-axis, from -10 to -70).

$$CH + H_2O \rightarrow CO + \tfrac{3}{2} H_2 \quad \Delta H_r^O = 28.1 \text{ kcal}$$

$$\Delta H_f^O (CH) = \tfrac{1}{6} \Delta H_f^O (C_6H_6)$$

$$\tfrac{3}{2} Me_p O_q + \tfrac{3}{2} H_2O \rightarrow$$
$$\tfrac{3}{2} Me_p O_{q+1} + \tfrac{3}{2} H_2$$

$$Fe_2O_3 \rightarrow Fe_3O_4$$

$$Co_3O_4 \rightarrow 3\,CO$$

$$MoO_3 \rightarrow MoO_2$$

$$\tfrac{3}{2} Me_p O_{q+1} + CH \rightarrow CO + \tfrac{1}{2} H_2O + \tfrac{3}{2} Me_p O_q$$

FIGURE 3

Figure showing HEAT OF REACTION IN SUB-REACTION kcal (y-axis, from -60 to 80) versus $\Delta H^o(O)$ kcal (x-axis, from -10 to -70).

$$CH + 2H_2O \rightarrow CO_2 + \frac{5}{2}H_2 \quad \Delta H_r^o = 18.25 \text{ kcal}$$

$$\Delta H_f^o(CH) = \frac{1}{6}\Delta H_f^o(C_6H_6)$$

$V_2O_5 \rightarrow V_2O_4$

$Fe_2O_3 \rightarrow Fe_3O_4$

$V_2O_4 \rightarrow V_2O_3$

$MoO_3 \rightarrow MoO_2$

$$2Me_pO_q + 2H_2O \rightarrow$$
$$2Me_pO_{q+1} + 2H_2$$

$$2Me_pO_{q+1} + CH \rightarrow$$
$$CO_2 + \frac{1}{2}H_2 + 2Me_pO_q$$

$$2Me_pO_q + O_2 \rightarrow$$
$$2Me_pO_{q+1}$$

FIGURE 4

FIGURE 5

Graph: HEAT OF REACTION IN SUB-REACTION kcal (y-axis) vs $\Delta H_O(O)$ kcal (x-axis)

$$CHS_{\frac{1}{4}} + \frac{5}{2}H_2O \rightarrow \frac{1}{4}SO_2 + CO_2 + 3H_2 \qquad \Delta H_r^0 = 24.8 \text{ kcal}$$

$$\frac{5}{2}Me_pO_q + \frac{5}{2}H_2O \rightarrow \frac{5}{2}Me_pO_{q+1} + \frac{5}{2}H_2$$

$$CHS_{\frac{1}{4}} + \frac{5}{2}Me_pO_{q+1} \rightarrow$$

$$\frac{1}{4}SO_2 + CO_2 + \frac{1}{2}H_2 + \frac{5}{2}Me_pO_q$$