Free energy
The driving force o f a chemical reaction

By

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- A system, including chemical reactions at constant pressure, which turns heat energy into mechanical energy is a form of heat engine.
- It is never practically possible to obtain maximum work, i.e. 100% efficiency, from such a device.
- Hence, of the total enthalpy (heat content) of the system only a part can be converted into useful work, this fraction of the total enthalpy being called the free energy, G.
- As with H, absolute values of G cannot be measured, only changes in free energy, ΔG.
- This new function ΔG, can be defined in terms of ΔH, ΔS and T, the temperature at which the reaction occurs and is a measure of the feasibility of a reaction.

The Gibbs-Helmholtz equation

The relationship between *ΔH, ΔS* and *ΔG* may be deduced as follows.

$$\underset{\text{enthalpy change}}{\Delta H^{\ominus}} - \underset{\text{energy available to do work}}{\Delta G^{\ominus}} = \underset{\text{unavailable energy used to cause disorder}}{T\Delta S^{\ominus}}$$

This may be rearranged:

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

$$\Delta G = \Delta H - T\Delta S$$

This important relationship is sometimes referred to as the Gibbs-Helmholtz equation (or the second law equation) and *ΔG* is a measure of the work obtainable from a reversible, isothermal process occurring at constant pressure and gives a direct indication of the possibility of chemical reaction.

Reactions tend to go in the direction which results in a decrease in free energy which means that the feasibility (Spontaneity) of reaction may now be defined as follows:

(i) if ΔG is negative a reaction is feasible;
(ii) if ΔG is positive a reaction is not feasible;
(iii) if ΔG is zero an equilibrium mixture is obtained, i.e. equal feasibility for both the forward and reverse reactions.

For a reaction at constant volume and constant temperature, the Helmholtz free energy change, ΔA, defined as

$$\Delta A = \Delta U - T\Delta S$$

Can be used as Criterion of Spontaneity

Example

Calculate $\Delta G^{\ominus}$ for the following reductions at 500 K by using the data provided and equation (2.22):

(i) $\mathrm{CuO(s)} + \mathrm{H_2(g)} \longrightarrow \mathrm{Cu(s)} + \mathrm{H_2O(g)}$ at 500 K

$$\Delta H^{\ominus}_{500} = -87\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta S^{\ominus}_{500} = +47\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

that is,

$$\Delta G^{\ominus} = -87\ 000 - (500 \times 47)\ \mathrm{J\ mol^{-1}}$$

$$= -110.5\ \mathrm{kJ\ mol^{-1}}$$

Since $\Delta G^{\ominus}$ is negative (and, incidentally, fairly large) the reaction is feasible at 500 K.

(ii) $\mathrm{ZnO(s)} + \mathrm{H_2(g)} \longrightarrow \mathrm{Zn(s)} + \mathrm{H_2O(g)}$ at 500 K

$$\Delta H^{\ominus}_{500} = +104\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta S^{\ominus}_{500} = +60\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

that is,

$$\begin{aligned}\Delta G^{\ominus} &= +104\,000 - (500 \times 60)\ \mathrm{J\ mol^{-1}} \\ &= +74\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Since $\Delta G^{\ominus}$ is positive the reaction cannot occur at 500 K.

The effect of temperature on the feasibility of a reaction

The value of ΔG depends on whether *ΔS* is positive or negative; a low temperature makes *TΔS* small and vice versa.

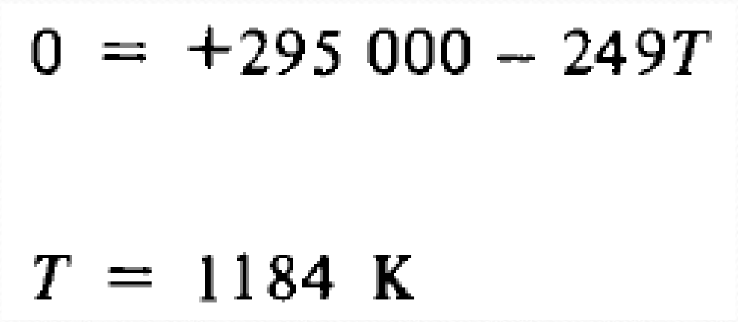
Consider the following reaction at say 1180 K, the boiling point of zinc:

$$\mathrm{ZnO(s)} + \mathrm{C(s)} \longrightarrow \mathrm{Zn(g)} + \mathrm{CO(g)}$$

$$\begin{aligned}\Delta H^{\ominus}_{T} &= +295\ \mathrm{kJ\ mol^{-1}} \\ \Delta S^{\ominus}_{T} &= +249\ \mathrm{J\ K^{-1}\ mol^{-1}}\end{aligned}$$

Substituting approximate, averaged values for *ΔH°* and *ΔS°* and assuming that the temperature of reversal, *T,* occurs when *ΔG°* = 0

this reversal temperature may be calculated

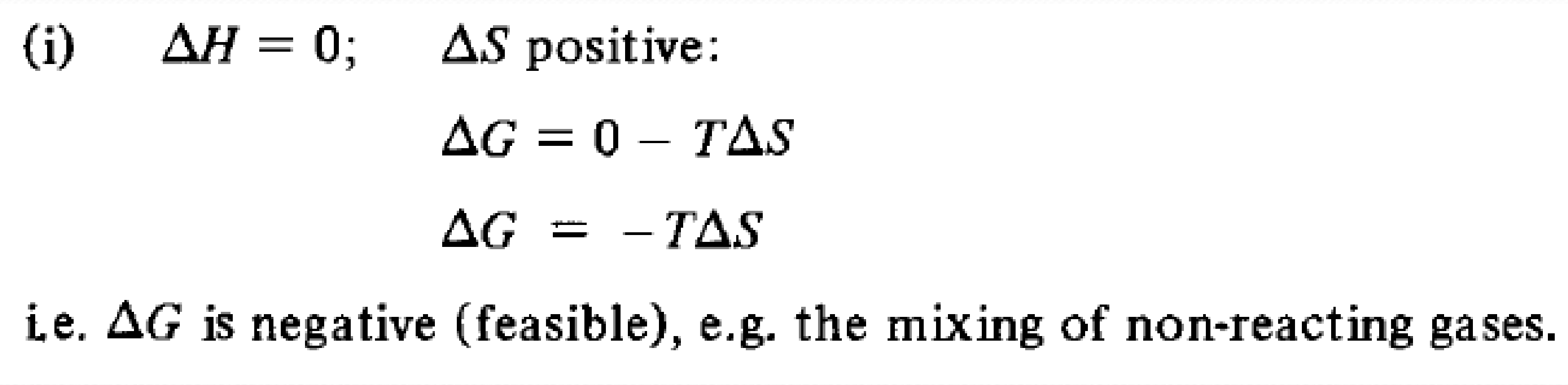


$$0 = +295\,000 - 249T$$

$$T = 1184 \text{ K}$$

Thus, within the accuracies used: if T < 1184 K, ΔG° is positive, and so the reaction cannot occur; but if $T > 1184$ K, ΔG° is negative, and the reaction can proceed.

Summary of the effect of the sign and magnitude of ΔH, ΔS and T on ΔG:



(i) $\Delta H = 0$; ΔS positive:

$$\Delta G = 0 - T\Delta S$$

$$\Delta G = -T\Delta S$$

i.e. ΔG is negative (feasible), e.g. the mixing of non-reacting gases.

(ii) ΔH negative or positive; $\Delta S = 0$:

$$\Delta G = \Delta H \qquad \text{(feasible if } -\Delta H\text{)}$$

i.e. reactions occurring at 0 K or when entropy remains constant, e.g.

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

(iii) ΔH negative; ΔS positive:

$$\Delta G = \Delta H - T\Delta S$$

Both ΔH and $-T\Delta S$ terms are negative giving a negative ΔG at all temperatures (feasible), i.e. exothermic reactions involving entropy increases, e.g.

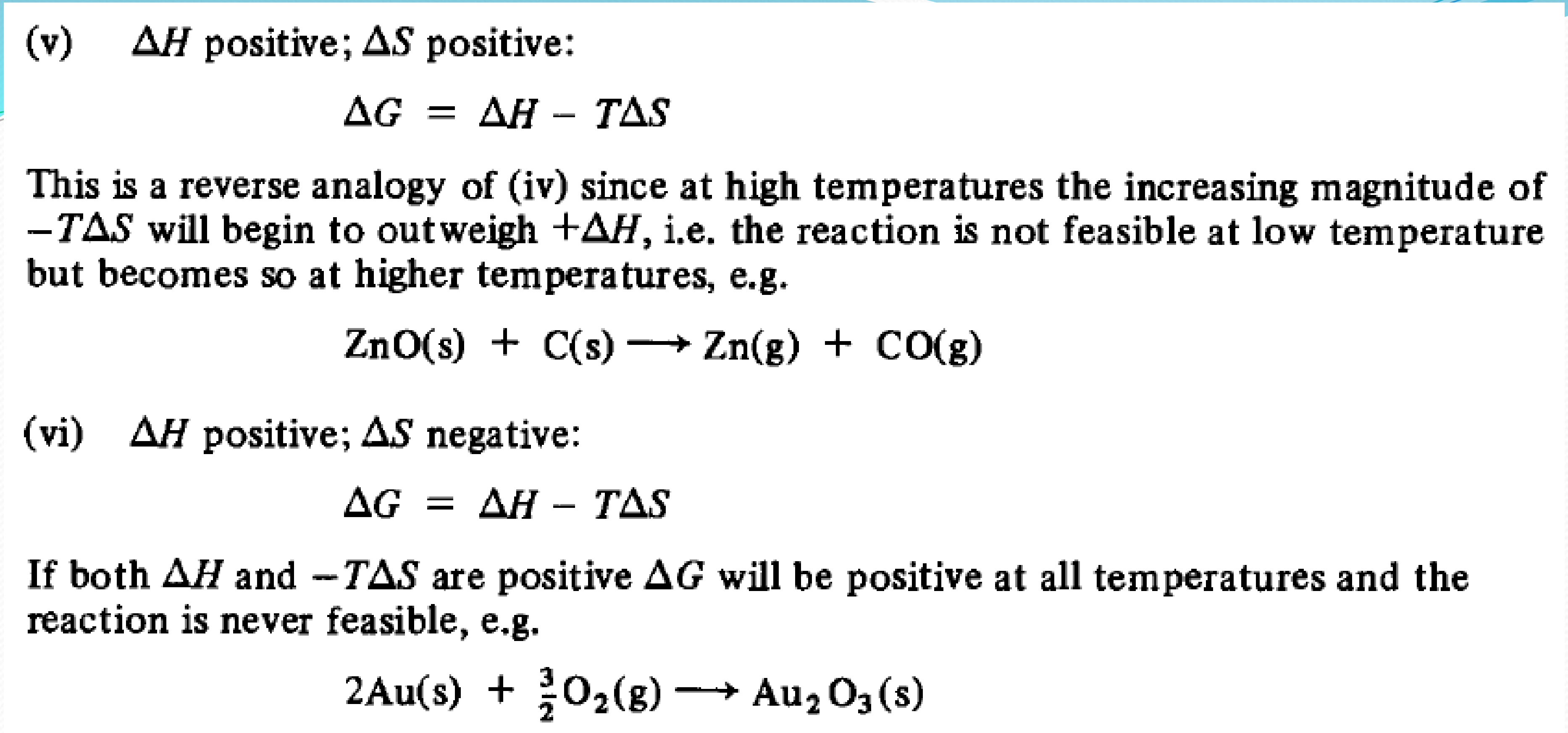
$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g)$$

(iv) ΔH negative; ΔS negative:

$$\Delta G = \Delta H - T\Delta S$$

ΔH is negative but $-T\Delta S$ is positive as $-T(-\Delta S) = T\Delta S$. Thus at low temperatures $-\Delta H$ exceeds $+T\Delta S$ in magnitude but at higher temperatures the increasingly larger $T\Delta S$ will eventually outweigh $-\Delta H$. Hence, the reaction is feasible at low temperatures but not at higher temperatures, e.g.

$$2Ag(s) + \tfrac{1}{2}O_2(g) \longrightarrow Ag_2O(s)$$



(v) ΔH positive; ΔS positive:

$$\Delta G = \Delta H - T\Delta S$$

This is a reverse analogy of (iv) since at high temperatures the increasing magnitude of $-T\Delta S$ will begin to outweigh $+\Delta H$, i.e. the reaction is not feasible at low temperature but becomes so at higher temperatures, e.g.

$$ZnO(s) + C(s) \longrightarrow Zn(g) + CO(g)$$

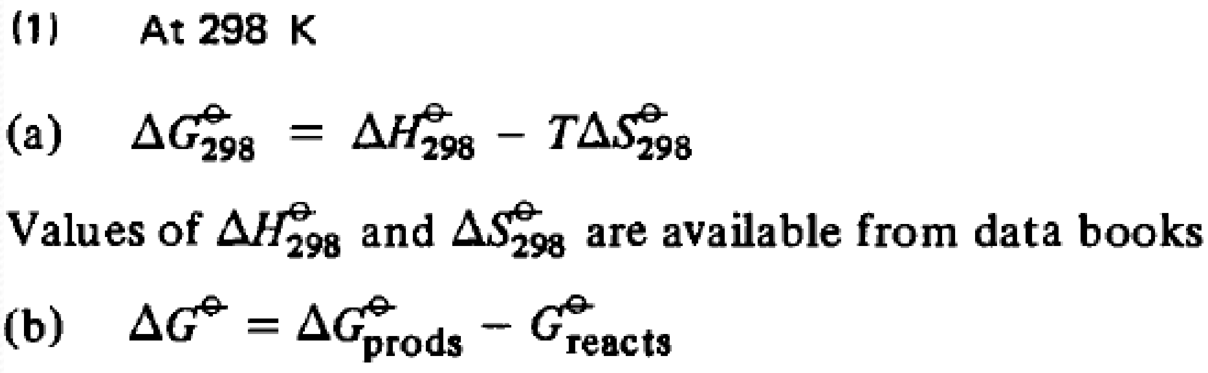
(vi) ΔH positive; ΔS negative:

$$\Delta G = \Delta H - T\Delta S$$

If both ΔH and $-T\Delta S$ are positive ΔG will be positive at all temperatures and the reaction is never feasible, e.g.

$$2Au(s) + \tfrac{3}{2}O_2(g) \longrightarrow Au_2O_3(s)$$

Calculating ΔG for reactions



(1) At 298 K

(a) $\Delta G^\ominus_{298} = \Delta H^\ominus_{298} - T\Delta S^\ominus_{298}$

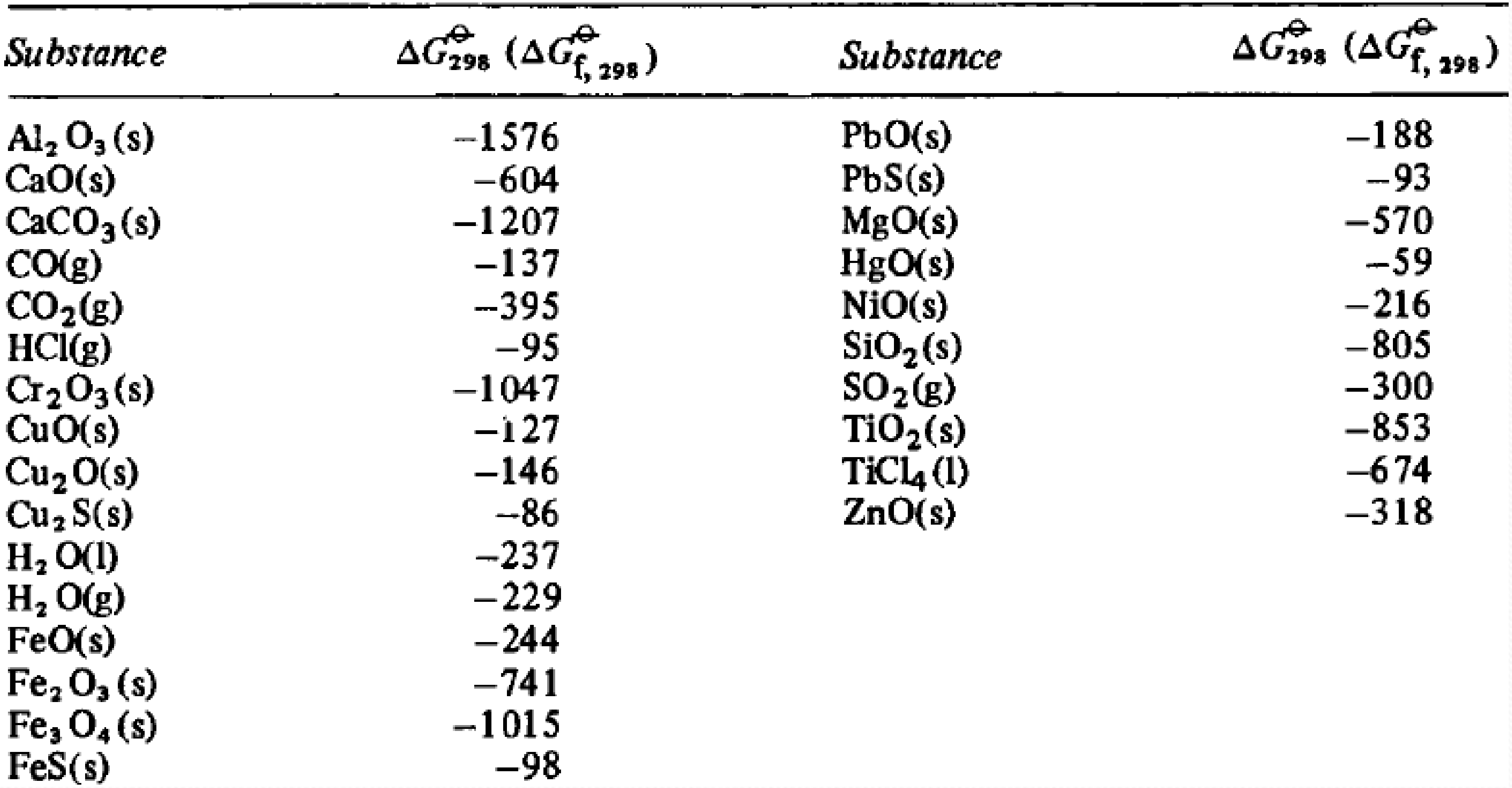
Values of $\Delta H^\ominus_{298}$ and $\Delta S^\ominus_{298}$ are available from data books

(b) $\Delta G^\ominus = \Delta G^\ominus_{\text{prods}} - G^\ominus_{\text{reacts}}$

- The standard free energy for elements, is taken to be zero

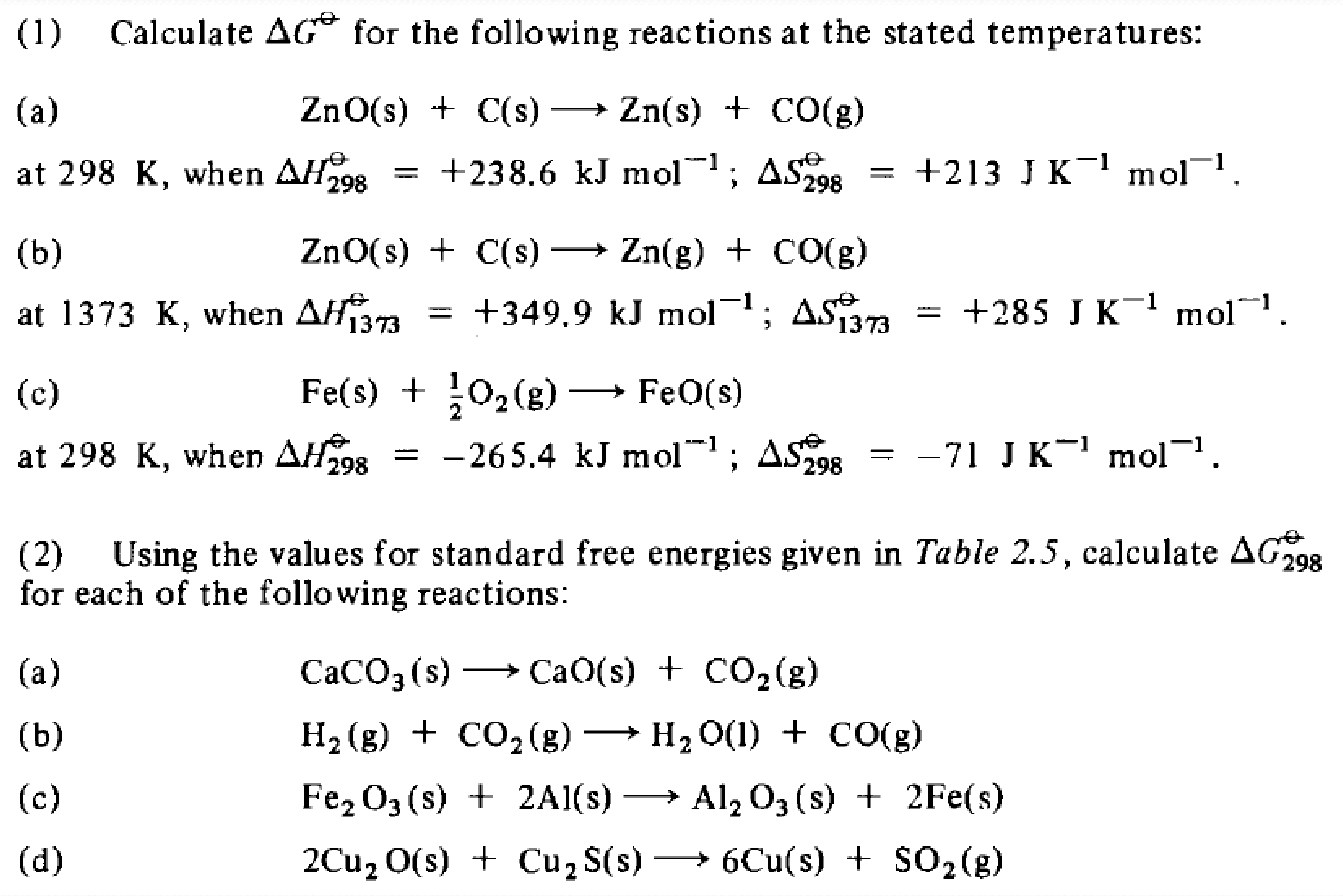
(2) At any temperature, T

$$\Delta G^{\ominus}_{T} = \Delta H^{\ominus}_{T} - T\Delta S^{\ominus}_{T}$$



Substance	$\Delta G^{\ominus}_{298}$ ($\Delta G^{\ominus}_{f,298}$)	Substance	$\Delta G^{\ominus}_{298}$ ($\Delta G^{\ominus}_{f,298}$)
$Al_2O_3(s)$	−1576	$PbO(s)$	−188
$CaO(s)$	−604	$PbS(s)$	−93
$CaCO_3(s)$	−1207	$MgO(s)$	−570
$CO(g)$	−137	$HgO(s)$	−59
$CO_2(g)$	−395	$NiO(s)$	−216
$HCl(g)$	−95	$SiO_2(s)$	−805
$Cr_2O_3(s)$	−1047	$SO_2(g)$	−300
$CuO(s)$	−127	$TiO_2(s)$	−853
$Cu_2O(s)$	−146	$TiCl_4(l)$	−674
$Cu_2S(s)$	−86	$ZnO(s)$	−318
$H_2O(l)$	−237		
$H_2O(g)$	−229		
$FeO(s)$	−244		
$Fe_2O_3(s)$	−741		
$Fe_3O_4(s)$	−1015		
$FeS(s)$	−98		

Home work



(1) Calculate $\Delta G^\ominus$ for the following reactions at the stated temperatures:

(a) $ZnO(s) + C(s) \longrightarrow Zn(s) + CO(g)$

at 298 K, when $\Delta H^\ominus_{298} = +238.6$ kJ mol^{-1}; $\Delta S^\ominus_{298} = +213$ J K^{-1} mol^{-1}.

(b) $ZnO(s) + C(s) \longrightarrow Zn(g) + CO(g)$

at 1373 K, when $\Delta H^\ominus_{1373} = +349.9$ kJ mol^{-1}; $\Delta S^\ominus_{1373} = +285$ J K^{-1} mol^{-1}.

(c) $Fe(s) + \frac{1}{2}O_2(g) \longrightarrow FeO(s)$

at 298 K, when $\Delta H^\ominus_{298} = -265.4$ kJ mol^{-1}; $\Delta S^\ominus_{298} = -71$ J K^{-1} mol^{-1}.

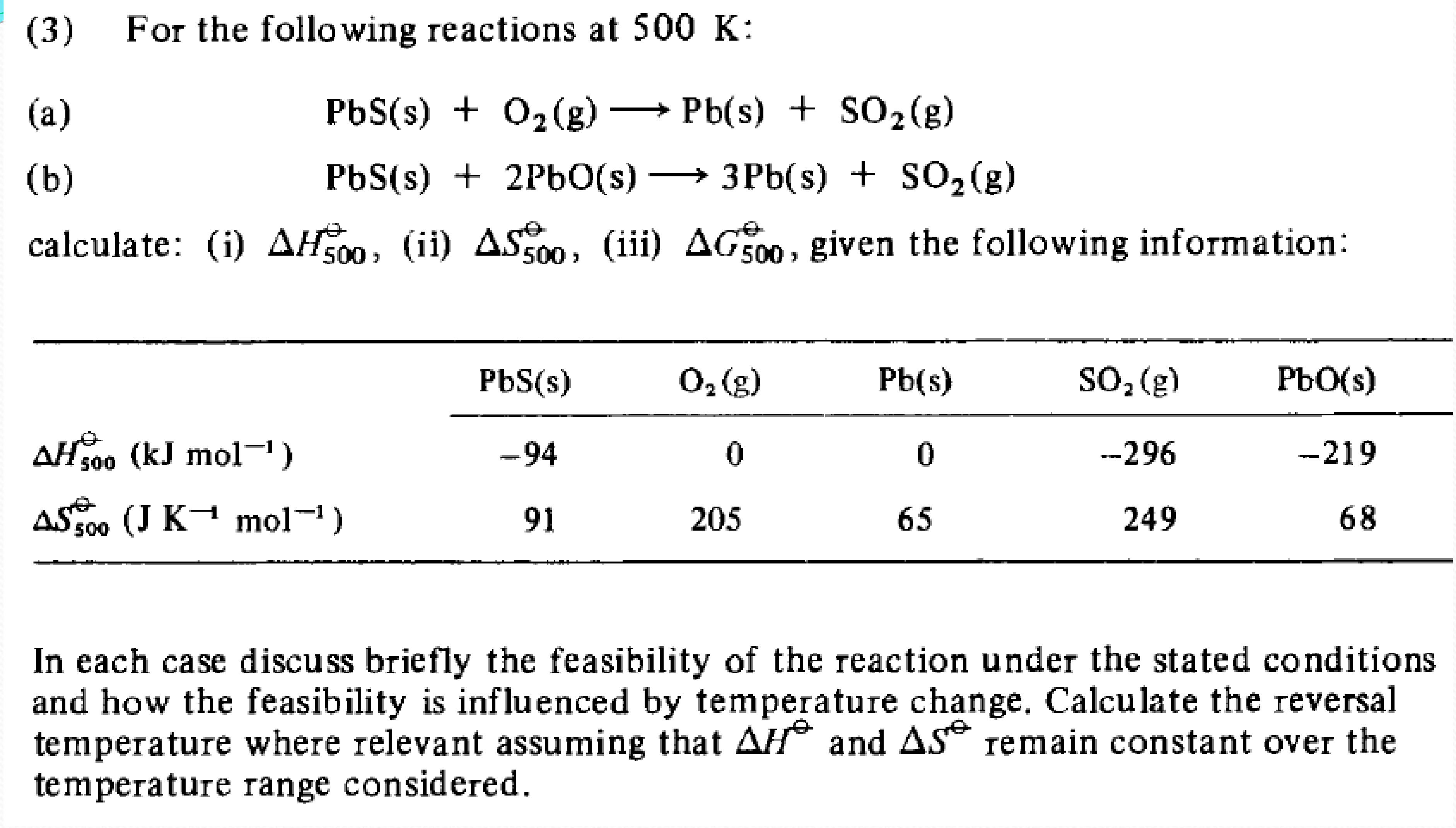
(2) Using the values for standard free energies given in *Table 2.5*, calculate $\Delta G^\ominus_{298}$ for each of the following reactions:

(a) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

(b) $H_2(g) + CO_2(g) \longrightarrow H_2O(l) + CO(g)$

(c) $Fe_2O_3(s) + 2Al(s) \longrightarrow Al_2O_3(s) + 2Fe(s)$

(d) $2Cu_2O(s) + Cu_2S(s) \longrightarrow 6Cu(s) + SO_2(g)$



(3) For the following reactions at 500 K:

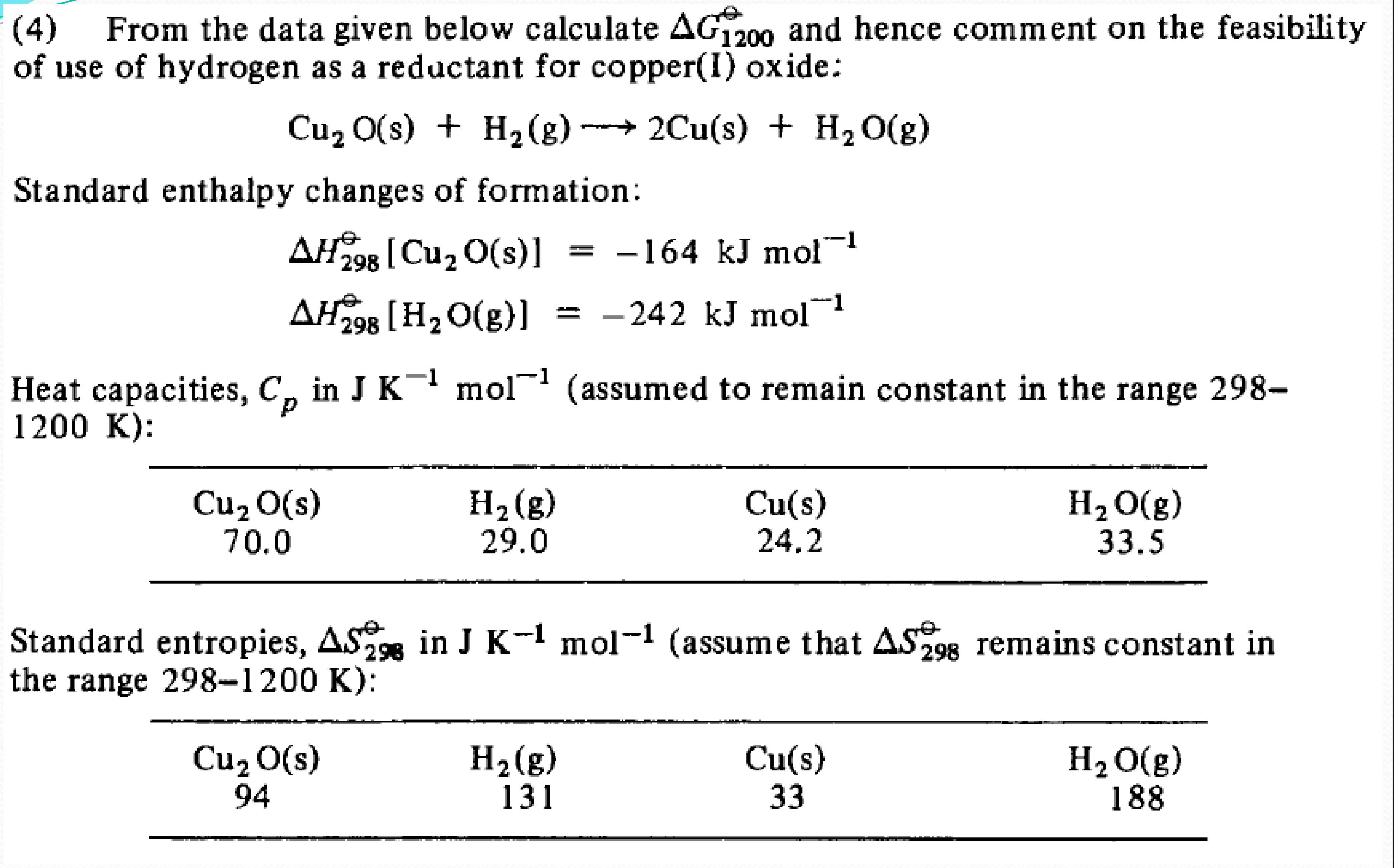
(a) $PbS(s) + O_2(g) \longrightarrow Pb(s) + SO_2(g)$

(b) $PbS(s) + 2PbO(s) \longrightarrow 3Pb(s) + SO_2(g)$

calculate: (i) $\Delta H^\ominus_{500}$, (ii) $\Delta S^\ominus_{500}$, (iii) $\Delta G^\ominus_{500}$, given the following information:

	$PbS(s)$	$O_2(g)$	$Pb(s)$	$SO_2(g)$	$PbO(s)$
$\Delta H^\ominus_{500}$ (kJ mol^{-1})	−94	0	0	−296	−219
$\Delta S^\ominus_{500}$ (J K^{-1} mol^{-1})	91	205	65	249	68

In each case discuss briefly the feasibility of the reaction under the stated conditions and how the feasibility is influenced by temperature change. Calculate the reversal temperature where relevant assuming that $\Delta H^\ominus$ and $\Delta S^\ominus$ remain constant over the temperature range considered.



(4) From the data given below calculate $\Delta G^{\ominus}_{1200}$ and hence comment on the feasibility of use of hydrogen as a reductant for copper(I) oxide:

$$Cu_2O(s) + H_2(g) \longrightarrow 2Cu(s) + H_2O(g)$$

Standard enthalpy changes of formation:

$$\Delta H^{\ominus}_{298}[Cu_2O(s)] = -164 \text{ kJ mol}^{-1}$$

$$\Delta H^{\ominus}_{298}[H_2O(g)] = -242 \text{ kJ mol}^{-1}$$

Heat capacities, C_p in J K^{-1} mol^{-1} (assumed to remain constant in the range 298–1200 K):

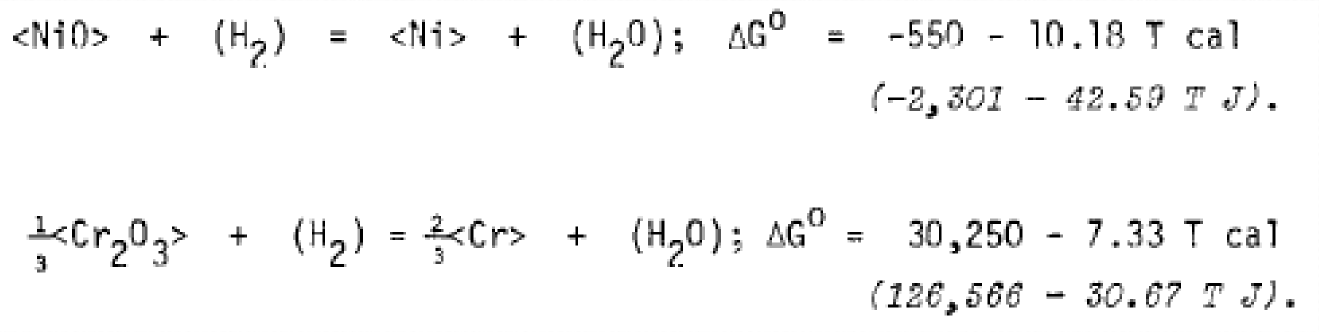
$Cu_2O(s)$	$H_2(g)$	$Cu(s)$	$H_2O(g)$
70.0	29.0	24.2	33.5

Standard entropies, $\Delta S^{\ominus}_{298}$ in J K^{-1} mol^{-1} (assume that $\Delta S^{\ominus}_{298}$ remains constant in the range 298–1200 K):

$Cu_2O(s)$	$H_2(g)$	$Cu(s)$	$H_2O(g)$
94	131	33	188

Example (1)

Given the following data, determine which metal has the greater probability of oxidation in steam at 827°C *(1100 K)* and 1 atm Pressure



$$\langle NiO\rangle + (H_2) = \langle Ni\rangle + (H_2O);\quad \Delta G^o = -550 - 10.18\,T\ \text{cal}$$

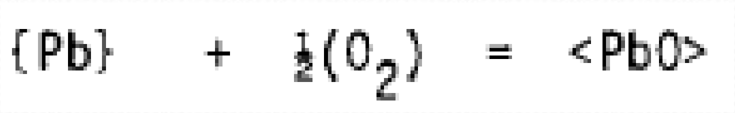
$$(-2{,}301 - 42.59\,T\ J).$$

$$\tfrac{1}{3}\langle Cr_2O_3\rangle + (H_2) = \tfrac{2}{3}\langle Cr\rangle + (H_2O);\quad \Delta G^o = 30{,}250 - 7.33\,T\ \text{cal}$$

$$(126{,}566 - 30.67\,T\ J).$$

Example (2)

Calculate the standard free energy change of the reaction



$$\{Pb\} + \tfrac{1}{2}(O_2) = \langle PbO\rangle$$

at 527°C *(800 K)* from the following data:

$\Delta H^{o}_{298,<PbO>} = -52,400$ cal/mole (

$S^{o}_{298,<PbO>} = 16.20$ cal/deg/mole

$S^{o}_{298,<Pb>} = 15.50$ cal/deg/mole

$S^{o}_{298,(O_2)} = 49.02$ cal/deg/mole

$C_{P,<PbO>} = 10.60 + 4.0 \times 10^{-3} T$ cal/deg/mole

$C_{P,<Pb>} = 5.63 + 2.33 \times 10^{-3} T$ cal/deg/mole

$C_{P,\{Pb\}} = 7.75 - 0.74 \times 10^{-3} T$ cal/deg/mole

$C_{P,(O_2)} = 7.16 + 1.0 \times 10^{-3} T - 0.4 \times 10^{5} T^{-2}$ cal/deg/mole

Melting point of Pb, $T_m = 327^{o}C$ *(600 K)*.

Latent heat of fusion of Pb, $L_f = 1,150$ cal/mole

Gibbs Free Energy and the Thermodynamic Functions

$G = H - TS$ or

$G = (U + PV) - TS$

Differentiating,

$dG = dU + PdV + VdP - TdS - SdT$

Since $dU = \delta q - PdV$,

and $dS = \delta q/T$ for a reversible change

Then $dU = TdS - PdV$

and dG becomes,

$$\mathbf{dG = VdP - SdT}$$

At constant pressure and variable temperature

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

At constant temperature and variable pressure,

$$\left(\frac{\partial G}{\partial P}\right)_T = V.$$

Similarly, for any reaction

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S,$$ and $$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V.$$

Gibbs-Helmholtz Equation

Since $\Delta G = \Delta H - T\,\Delta S$ and $\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S,$

Then $\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P.$

This is known as the Gibbs-Helmholtz equation, and could also be written in the following form:

$$\left[\frac{\partial(\Delta G/T)}{\partial T}\right]_P = -\frac{\Delta H}{T^2},$$

$$\left[\frac{\partial(\Delta G/T)}{\partial(1/T)}\right]_P = \Delta H.$$

Example (3)

Calculate the standard enthalpy and entropy "changes at 25°C *(298 K)* for the reaction

$$2\langle Cu\rangle + \tfrac{1}{2}(O_2) = \langle Cu_2O\rangle;$$

$$\Delta G^o = -40{,}500 - 3.92\,T\log T + 29.5\,T \text{ cal}$$

Example (4)

ΔG° for the reaction $\langle Ni\rangle + 1/2(O_2) \rightarrow \langle NiO\rangle$ at 25°C *(298 K)* is -50786 cal . Calculate ΔG° at 327°C *(600 K)* from the following data:

$$\Delta H^o_{298,\langle NiO\rangle} = -57{,}500 \text{ cal/mole}$$

$$C_{P,\langle NiO\rangle} = 12.91 \text{ cal/deg/mole}$$

$$C_{P,\langle Ni\rangle} = 6.03 + 10.44 \times 10^{-6}\,T^2 - 2.50 \times 10^{-3}\,T \text{ cal/deg/mole}$$

$$C_{P,(O_2)} = 7.16 + 1.0 \times 10^{-3}\,T - 0.4 \times 10^{5}\,T^{-2} \text{ cal/deg/mole}$$