

MME 2010 METALLURGICAL THERMODYNAMICS II

Reacting Systems with Variable Composition

Fundamental Property Relation for Systems of Variable Composition

$$d(nG) = (nV)dP - (nS)dT$$

Basic relation connecting the Gibbs free energy to the temperature and pressure of any closed system

For the case of an *open system*, nG is still a function of T and P , and also a function of the number of moles of each chemical species since material may be taken from or added to the system

$$nG = g(P, T, n_1, , n_2, , n_3, \dots n_i)$$

differentiating:

$$d(nG) = \underbrace{\left[\frac{\delta(nG)}{\delta P} \right]_{T,n}}_{(nV)} dP + \underbrace{\left[\frac{\delta(nG)}{\delta T} \right]_{P,n}}_{-(nS)} dT + \sum_i \underbrace{\left[\frac{\delta(nG)}{\delta n_i} \right]_{P,T,n_j}}_{(\mu_i)}$$

$$d(nG) = (nV)dP - (nS)dT + \sum \mu_i dn_i$$

Consider a closed system consisting of two phases that are considered open systems

$$d(nG)^\alpha = (nV)^\alpha dP - (nS)^\alpha dT + \sum \mu_i^\alpha dn_i^\alpha$$
$$d(nG)^\beta = (nV)^\beta dP - (nS)^\beta dT + \sum \mu_i^\beta dn_i^\beta$$

A total-system property is expressed by an equation of the following form:

$$nM = (nM)^\alpha + (nM)^\beta$$

so

$$d(nG) = (nV)dP - (nS)dT + \sum \mu_i^\alpha dn_i^\alpha + \sum \mu_i^\beta dn_i^\beta$$

Since the two-phase system is closed the constant composition form also holds

$$d(nG) = (nV)dP - (nS)dT$$

Thus at equilibrium

$$\sum \mu_i^\alpha dn_i^\alpha + \sum \mu_i^\beta dn_i^\beta = 0$$

The changes dn_i^α and dn_i^β result from mass transfer between phases so that

$$dn_i^\alpha = -dn_i^\beta \quad \sum (\mu_i^\alpha - \mu_i^\beta) dn_i^\alpha = 0$$

Thus multiple phases at the same T and P are in equilibrium when the chemical potential of each species is the same for all phases

$$\mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\pi \quad (i = 1, 2, \dots, N)$$

Chemical potential of a chemical species in a solution is given as:

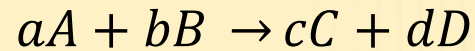
$$\mu_i = G_i + RT \ln a_i$$

Where a_i is the activity of chemical species i , which is proportional to its partial pressure P_i

Mole fraction replaces activity coefficient in ideal solutions

Chemical potential is a criteria for equilibrium in reacting systems

Consider a general reaction in equilibrium:



Consider the reaction in a closed mixture of ideal gases at constant temperature

The change in Gibbs free energy of each ideal gas component as a function of its pressure is given as

$$\frac{\partial G_i}{\partial P_i} = V_i$$

$$dG_i = \frac{RTdP_i}{P_i}$$

$$\int dG_i = \int \frac{RT dP_i}{P_i}$$

$$G_i = G_i^o + RT \ln \frac{P_i}{P_i^o}$$

The change in free energy of the system at constant temperature is the sum of the free energy change of its components

$$nG = \sum n_i G_i$$

$$d(nG) = \sum n_i dG_i + \sum G_i dn_i$$

$$\Delta(nG) = \sum \frac{RTn_i}{P_i} dP_i + \sum G_i dn_i$$

Since mole number and pressure of ideal gases are proportional, n_i / P_i is constant and since the total pressure of the system is constant, $\sum dP_i = 0$

$$\Delta G = \sum G_i dn_i$$

In the case of system equilibrium

$$\Delta G = \sum G_i dn_i = 0$$

$$\Delta G = \sum G_i^o dn_i + RT \sum \ln(P_i dn_i)$$

The stoichiometric coefficients a, b, c, d of each component in the ideal gas mixture can be used to represent dn_i :

$$cG_C^o + dG_D^o - aG_A^o - bG_B^o + RT \ln P_C^c + RT \ln P_D^d + RT \ln P_A^{-a} + RT \ln P_B^{-b} = 0$$

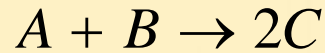
$$\Delta G^o + RT \ln \frac{P_C^c P_D^d}{P_A^a P_B^b} = 0$$

where $\Delta G^o = cG_C^o + dG_D^o - aG_A^o - bG_B^o$

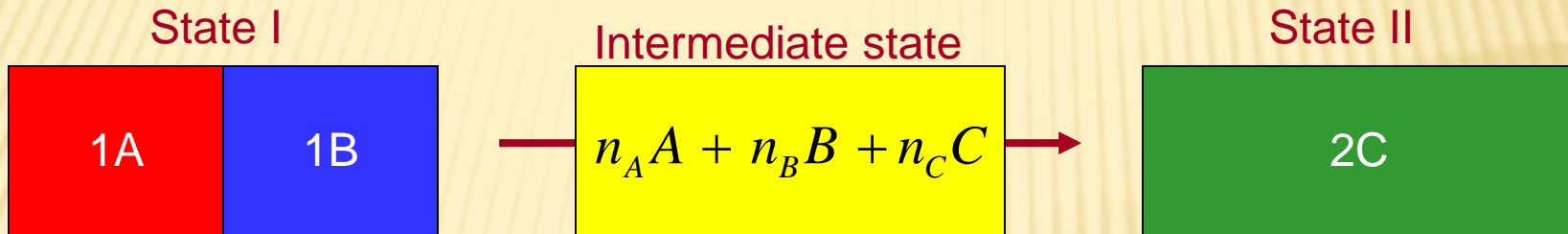
Absolute Gibbs free energy is computed for gas phases as:

$$G_i = G_i^o + RT \ln P_i$$

Consider a simple chemical reaction:



$$\begin{aligned}\Delta G^\circ &= G_{II} - G_I \\ &= 2G_C^\circ - G_A^\circ - G_B^\circ\end{aligned}$$



$$G = n_A \mu_A + n_B \mu_B + n_C \mu_C = n_A \mu_A + n_A \mu_B + 2(1 - n_A) \mu_C$$

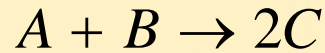
Recall: $\mu_i = G_i^\circ + RT \ln a_i$

$$\begin{aligned}G &= n_A (G_A^\circ + RT \ln a_A) + n_A (G_B^\circ + RT \ln a_B) + 2(1 - n_A) (G_C^\circ + RT \ln a_C) \\ &= n_A G_A^\circ + n_A G_B^\circ + 2(1 - n_A) G_C^\circ + RT [n_A \ln a_A + n_A \ln a_B + 2(1 - n_A) \ln a_C]\end{aligned}$$

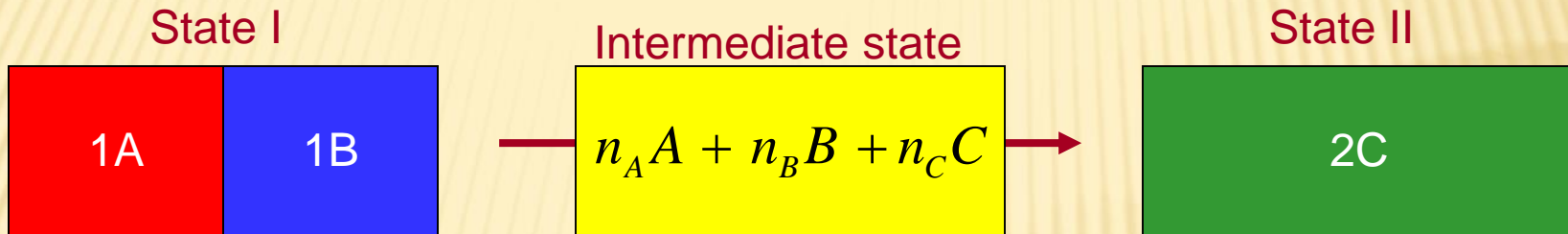
$$\frac{\partial G}{\partial n_A} = \underbrace{G_A^\circ + G_B^\circ - 2G_C^\circ}_{-\Delta G^\circ} + RT (\ln a_A + \ln a_B - 2 \ln a_C) = 0 \quad \text{Equilibrium condition}$$

$$\Delta G^\circ = RT (\ln a_A + \ln a_B - 2 \ln a_C)$$

Equilibrium condition



$$\begin{aligned}\Delta G^\circ &= G_{II} - G_I \\ &= 2G_C^\circ - G_A^\circ - G_B^\circ\end{aligned}$$



$$\Delta G^\circ = RT(\ln a_A + \ln a_B - 2 \ln a_C)$$

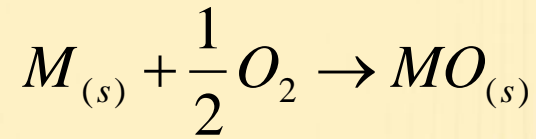
$$\Delta G^\circ = RT \ln \left(\frac{a_A a_B}{a_C^2} \right)$$

$$\Delta G^\circ = -RT \ln \left(\frac{a_C^2}{a_A a_B} \right)$$

$$\Delta G^\circ = -RT \ln K$$

K is defined as an
“Equilibrium Constant”

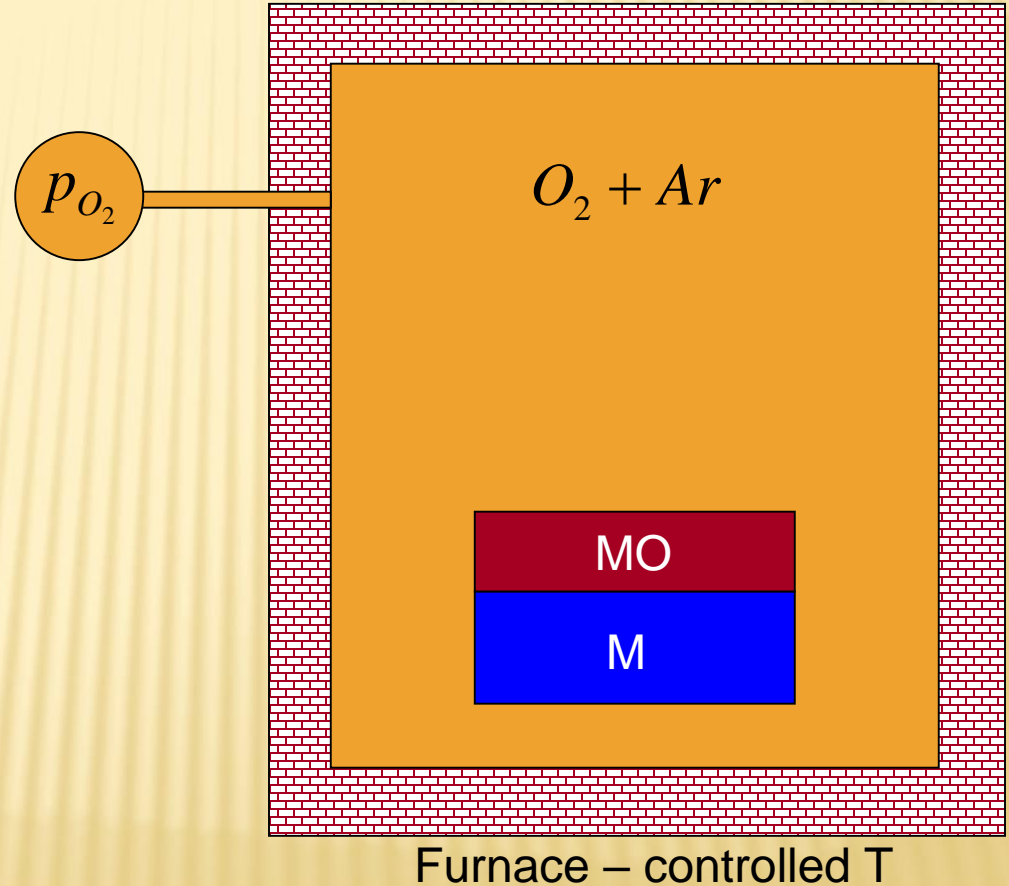
Example



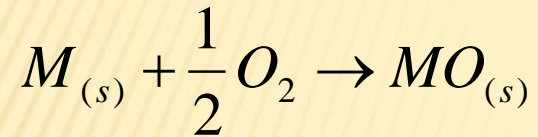
$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \frac{a_C^z}{a_A^x a_B^y}$$
$$= \frac{1}{p_{O_2}^{1/2}}$$

$$\Delta G^\circ = -RT \ln\left(\frac{1}{p_{O_2}}\right)^{\frac{1}{2}}$$

$$\Delta G^\circ = \frac{1}{2} RT \ln p_{O_2}$$



Example

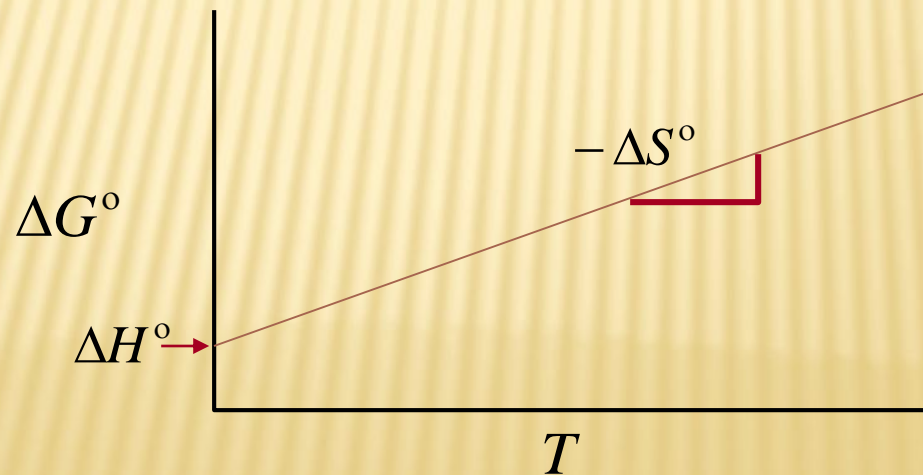


$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

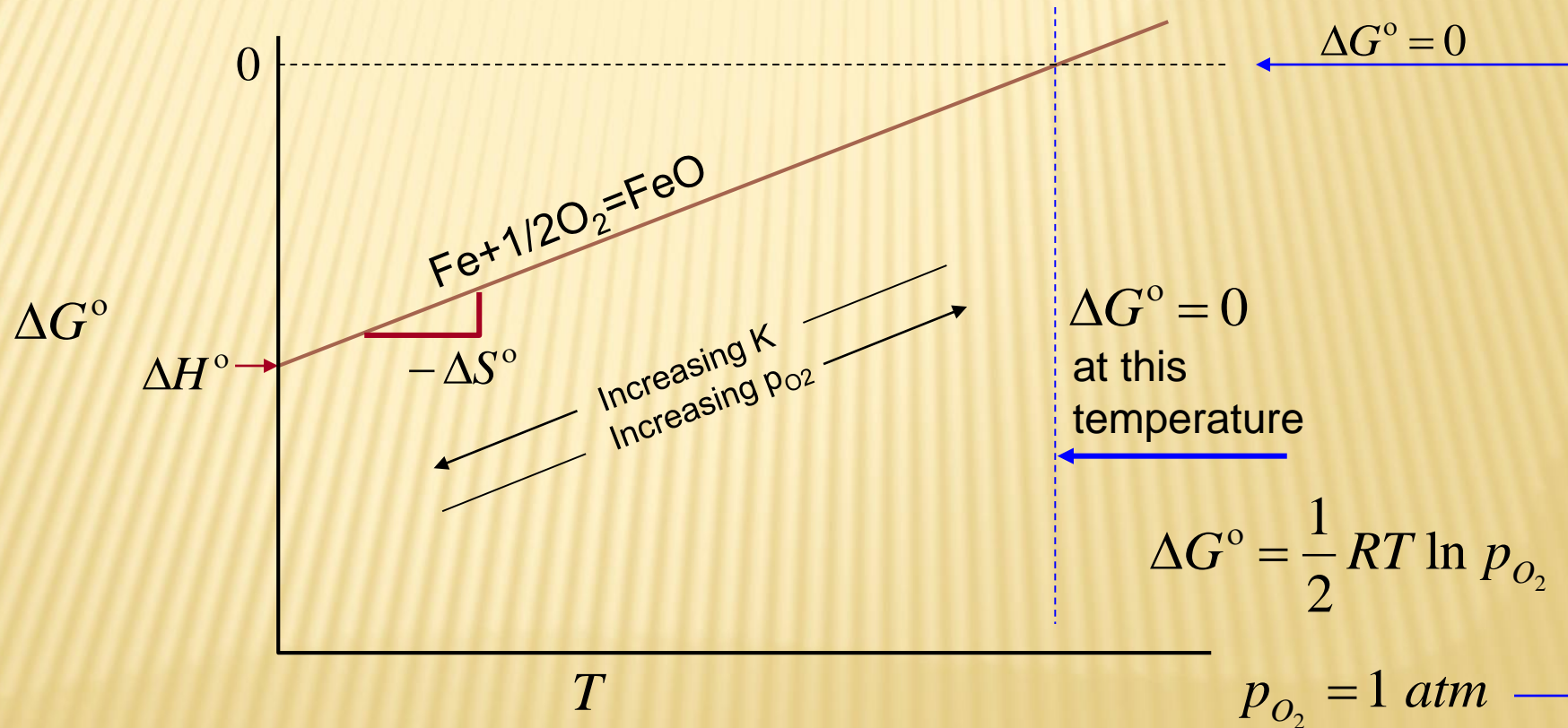
$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = \frac{1}{2} RT \ln p_{O_2}$$

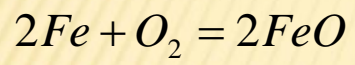
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$



Example 2

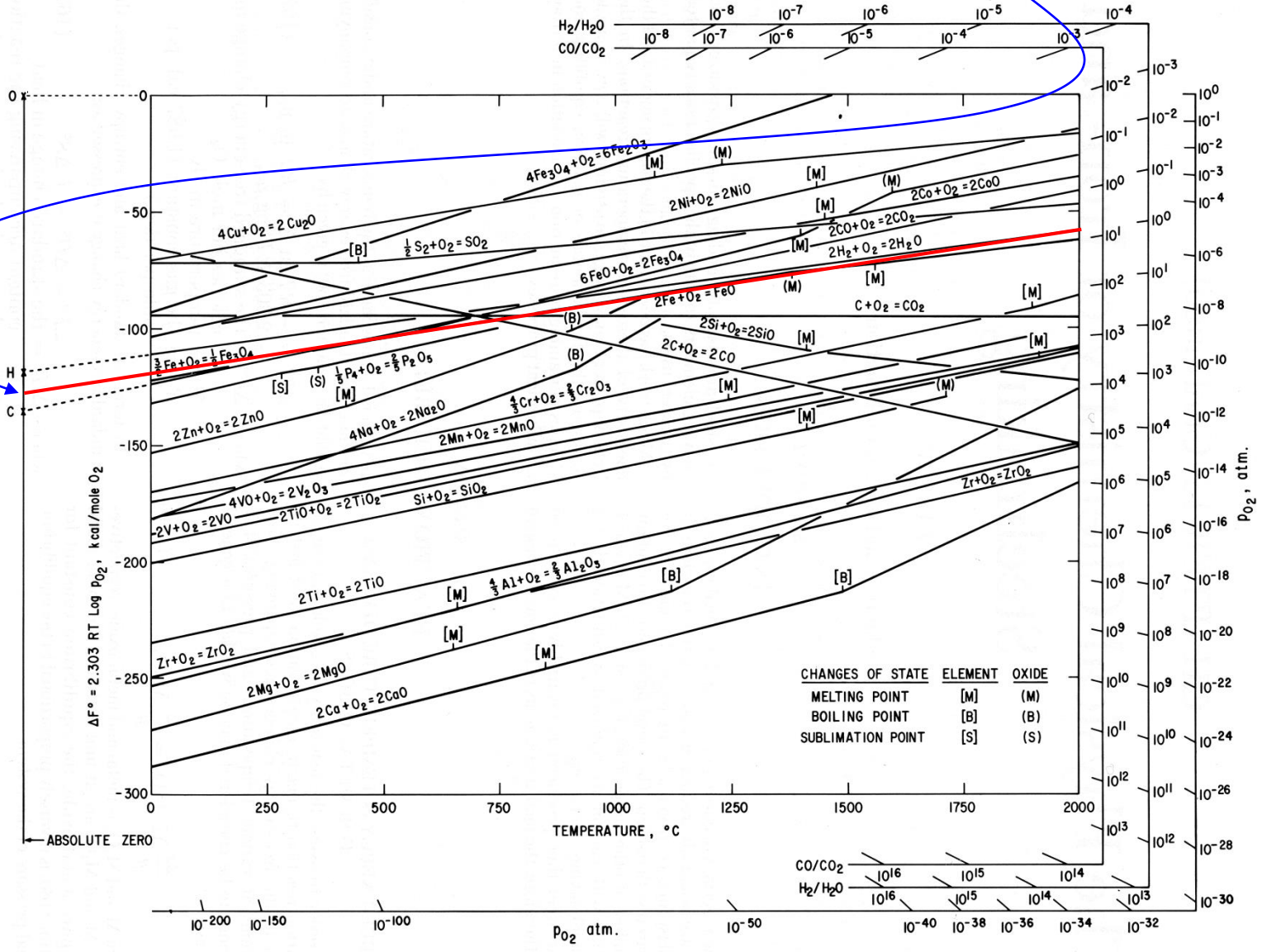


Using The Ellingham Diagram



$$\Delta G^\circ = -527,400 + 128.7T \quad (J)$$

$$\Delta G^\circ = -126,052 + 30.76T \quad (cal)$$



Using The Ellingham Diagram



$$\Delta G^\circ = -126,052 + 30.76T \quad (cal)$$

$$\Delta G^\circ = -RT \ln K$$

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$$

$$K = \frac{a_{FeO}^2}{a_{Fe}^2 a_{O_2}}$$

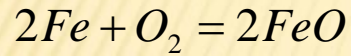
$$K = \frac{1}{p_{O_2}}$$

At T=1000 °C:

$$\begin{aligned} \Delta G^\circ &= -126,052 + 30.76(1273) \\ &= 86,895 \quad (cal/mol) \end{aligned}$$

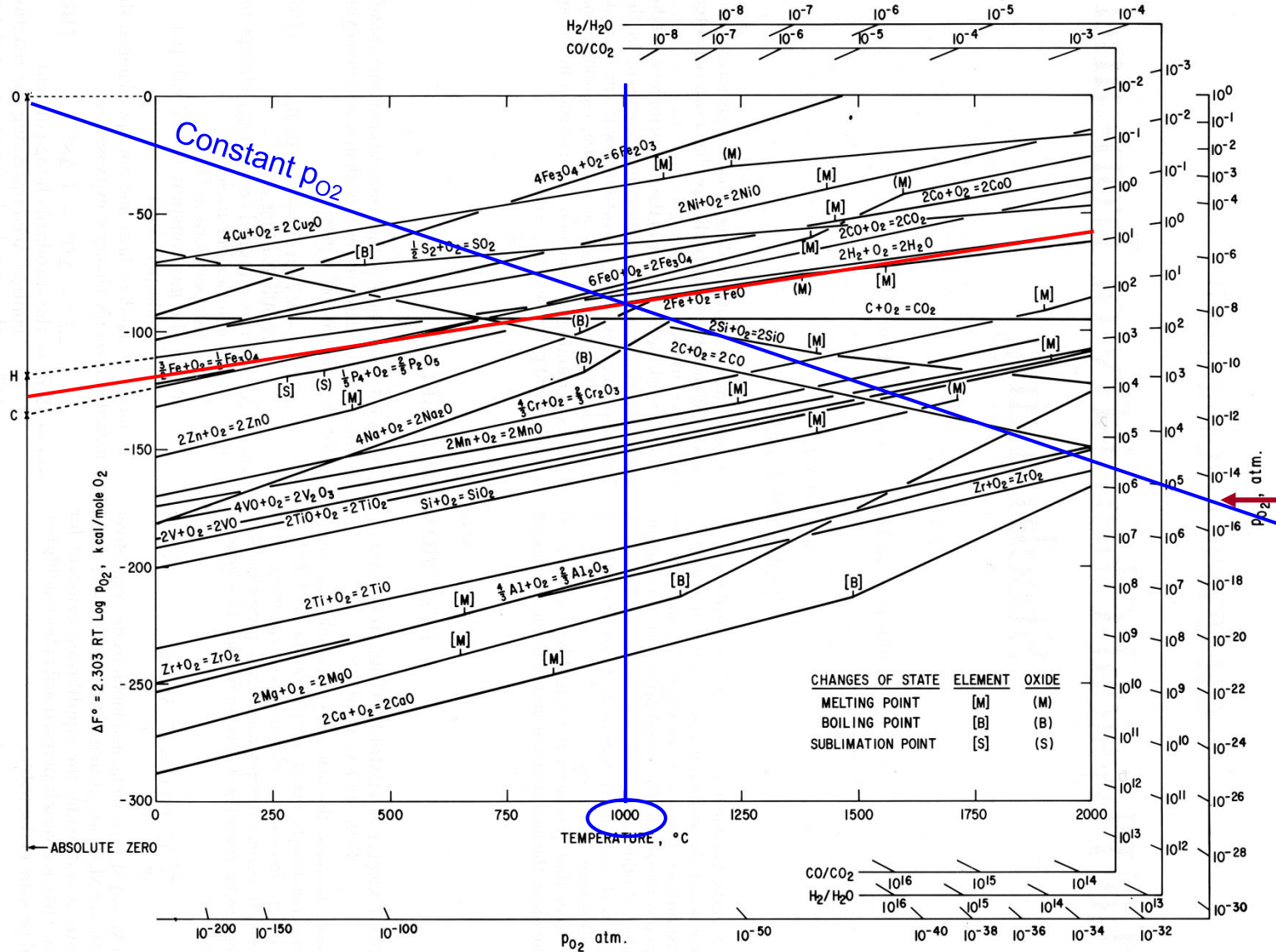
$$\begin{aligned} p_{O_2} &= \frac{1}{K} = \exp\left(\frac{\Delta G^\circ}{RT}\right) \\ &= \exp\left(\frac{-86895 \text{ cal/mol}}{(1.987 \text{ cal/K-mol})(1273 \text{ K})}\right) \\ &= 1.21 \times 10^{-15} \end{aligned}$$

Using The Ellingham Diagram



$$\Delta G^\circ = -527,400 + 128.7T \quad (J)$$

$$\Delta G^\circ = -126,052 + 30.76T \quad (cal)$$



$p_{O_2} \approx 10^{-15}$

Basis of the Ellingham Diagram

ΔG° for any system can be calculated for any temperature since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$,

$$\Delta G^\circ = \Delta H^\circ_{298} + \int_{298}^T \Delta C_P dT - T \left(\Delta S^\circ_{298} + \int_{298}^T \frac{\Delta C_P dT}{T} \right)$$

where $C_P = a + bT + \frac{c}{T^2}$

and $\Delta C_P = \Delta a + \Delta bT + \frac{\Delta c}{T^2}$ where $\Delta a, b, c = \sum \Delta a, b, c_{products} - \sum \Delta a, b, c_{reactants}$

$$\Delta G^\circ = \Delta H^\circ_{298} + \int_{298}^T \left(\Delta a + \Delta bT + \frac{\Delta c}{T^2} \right) dT - T \left(\Delta S^\circ_{298} + \int_{298}^T \frac{\left(\Delta a + \Delta bT + \frac{\Delta c}{T^2} \right) dT}{T} \right)$$

$$\Delta G^\circ = \Delta H^\circ_{298} + \left(\Delta aT + \frac{\Delta bT^2}{2} - \frac{\Delta c}{T} \right) \Big|_{298}^T - T \left(\Delta S^\circ_{298} + \left(\Delta a \ln T + \Delta bT - \frac{\Delta c}{2T^2} \right) \Big|_{298}^T \right)$$

Replacement of the upper and the lower limits yields

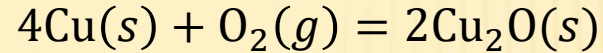
$$\Delta G^\circ = I_0 + I_1T - \Delta aT \ln T - \frac{\Delta b}{2}T^2 - \frac{\Delta c}{2T}$$

where $I_0 = \Delta H^\circ_{298} - \left(\Delta a298 + \frac{\Delta b298^2}{2} - \frac{\Delta c}{298} \right)$

$$I_1 = \Delta a - \Delta S^\circ_{298} + \Delta a \ln 298 + \Delta b298 - \frac{\Delta c}{2 \cdot 298^2}$$

Example - One important equilibrium between condensed phases such as metals and oxides and a gaseous phase such as oxygen is oxidation of metals

Consider the oxidation of copper



$$\Delta H^{\circ}_{298} = -334400 \text{ J}$$

$$\Delta S^{\circ}_{298} = -152.07 \text{ J/K}$$

$$\Delta C_p = 4.18 + 0.01839T + \frac{1.67 * 10^5}{T^2} \text{ J/K}$$

$$I_o = -334400 - 1500$$

$$I_1 = 4.18 + 152.07 + 28.35$$

Using the above thermochemical data

$$\Delta G^{\circ} = -335900 + 184.59T - 4.18T \ln T - 0.0092T^2 - \frac{0.84 * 10^5}{T} \text{ J}$$

Alternatively the standard free energy for formation of pure Cu_2O from pure Cu and oxygen is

$$\Delta G^\circ = RT \ln P_{\text{O}_2}(\text{eqm})$$

Experimental variation of ΔG° with T can be calculated from the measured oxygen partial pressure $P_{\text{O}_2}(\text{eqm})$ that is in equilibrium with Cu and Cu_2O

When experimental ΔG° vs T is fit to

$$\Delta G^\circ = A + BT \log T + CT$$

$$\Delta G^\circ = -338580 - 32.77T \log T + 246.62T \text{ J}$$

If a 2-term fit is used

$$\Delta G^\circ = A + BT$$

$$\Delta G^\circ = -328580 + 137.94T \text{ J}$$

The comparison of ΔG° calculated from the thermochemical data and experimental data is made, the difference in temperature range 400 to 1200 K is seen between 293 to 794 J

The comparison of ΔG° calculated from the experimental data and 2-term fit shows that the difference in the 400 to 1200 K temperature range is even less, between 286 to 788 J

T (K)	Thermochemical	Experimental	2-term fit	A-B	B-C	A-C
400	-273748	-274041	-273324	293	-717	-424
600	-244655	-245241	-245736	586	495	1081
800	-216566	-217360	-218148	794	788	1582
1000	-189480	-190274	-190560	794	286	1080
1200	-163270	-163689	-162972	419	-717	-298

Table shows that overall difference between ΔG° calculated from the thermochemical data and 2-term fit in the temperature range is at most 1.6 kJ which is within the experimental error for most of the ΔG° measurements

Therefore the variation of ΔG° with temperature for oxidation and sulfidation reactions can be approximated to linear forms

This observation lead to representation of the reaction free energies as Ellingham diagram:

Ellingham plotted the experimentally determined ΔG° values as a function of T for the oxidation and sulfidation of a series of metals

The general form of the relationships approximated to straight lines over temperature ranges in which no change in physical state occurred

The complex terms $T \ln T$, T^2 and $1/T$ does not affect the linearity of the curves for the considered range

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

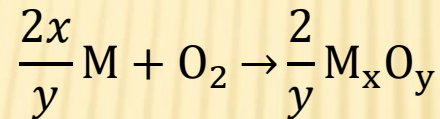
$$\Delta G^{\circ} = A + BT$$

A, which is the intercept at 0 K, is the temperature independent ΔH°

B, the slope, $-\Delta S^{\circ}$

These approximations imply that $\Delta C_p \approx 0$ for oxidation reactions

Another important characteristic of Ellingham diagram is that; all the lines represent reactions involving one mole of oxygen:



Therefore, the ordinate ΔG° of all the oxidation reactions become $RT \ln P_{O_2}(eqm)$

Almost all the ΔG° lines have positive slopes since $\Delta S^{\circ} < 0$:



$$\Delta S^{\circ} = \Delta S^{\circ}_{MO_2} - \Delta S^{\circ}_M - \Delta S^{\circ}_{O_2}$$

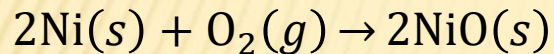
$S^{\circ}_{O_2}$ is generally dominant in the temperature range where M and MO_2 are solid

$$\text{So } \Delta S^{\circ} \approx -S^{\circ}_{O_2}$$

The slopes are approximately equal in the temperature range where metal and oxide are solid

Therefore almost all the lines are parallel to each other in this temperature range

Examples



$$S^\circ_{\text{O}_2} = 205.11 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$S^\circ_{\text{Ni}(s)} = 29.8 \frac{\text{J}}{\text{mol} \cdot \text{K}} \quad \text{Standard entropies at 298 K}$$

$$S^\circ_{\text{NiO}(s)} = 38.09 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$\Delta S^\circ = -188.53 \text{ J/K}$$

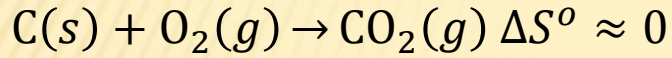


$$S^\circ_{\text{Sn}(s)} = 51.49 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

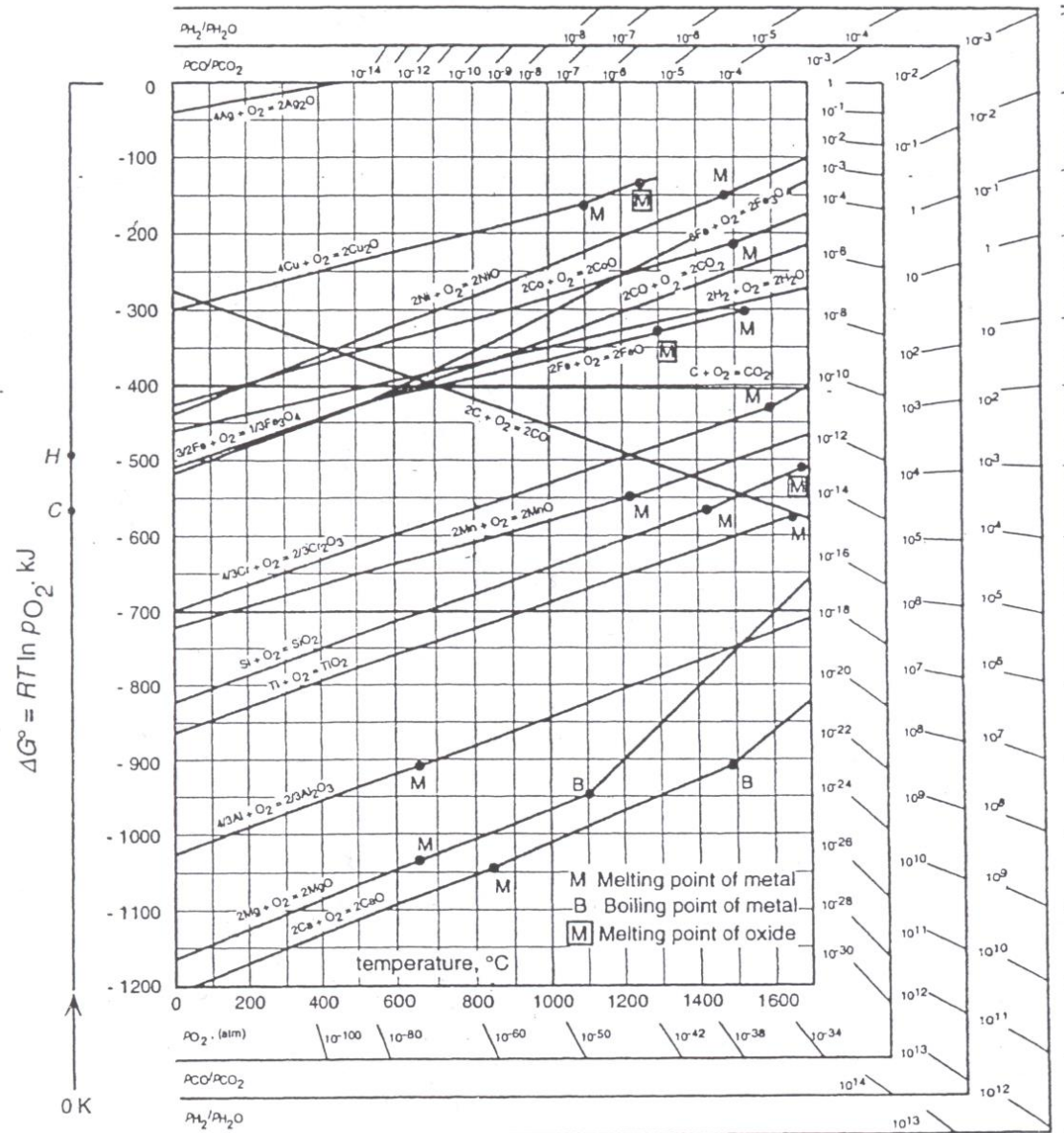
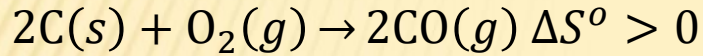
$$S^\circ_{\text{SnO}_2(s)} = 48.59 \frac{\text{J}}{\text{mol} \cdot \text{K}} \quad \text{Standard entropies at 298 K}$$

$$\Delta S^\circ = -208.04 \text{ J/K}$$

The exceptions to the general trends in oxidation lines are



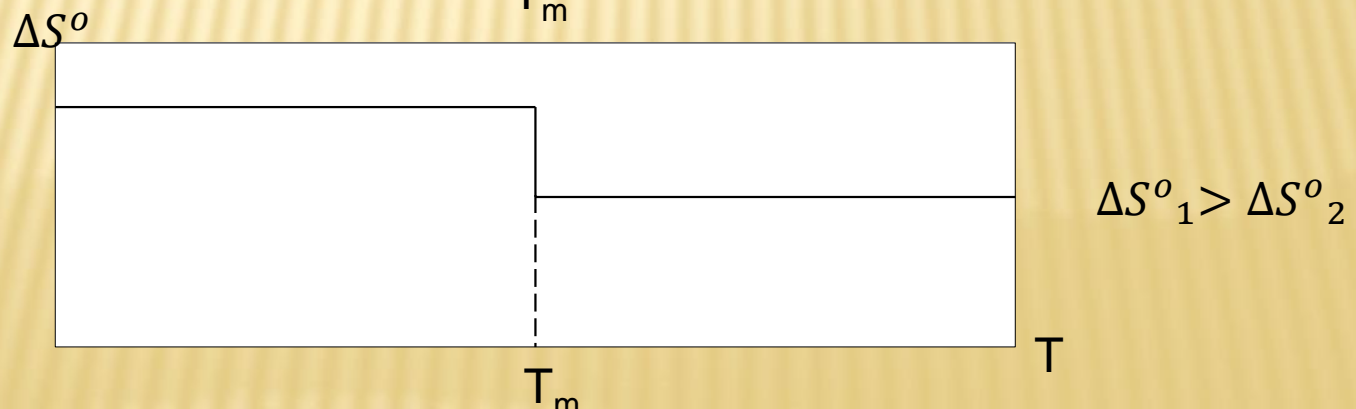
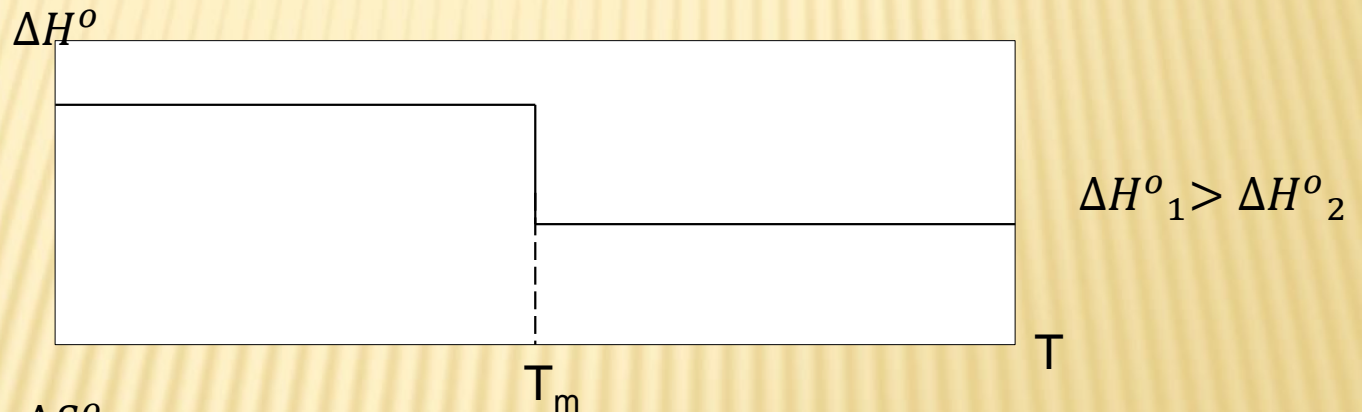
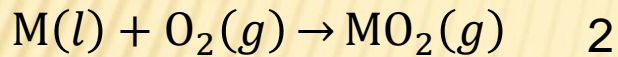
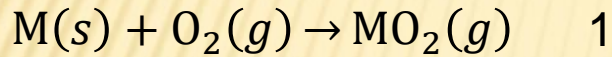
and



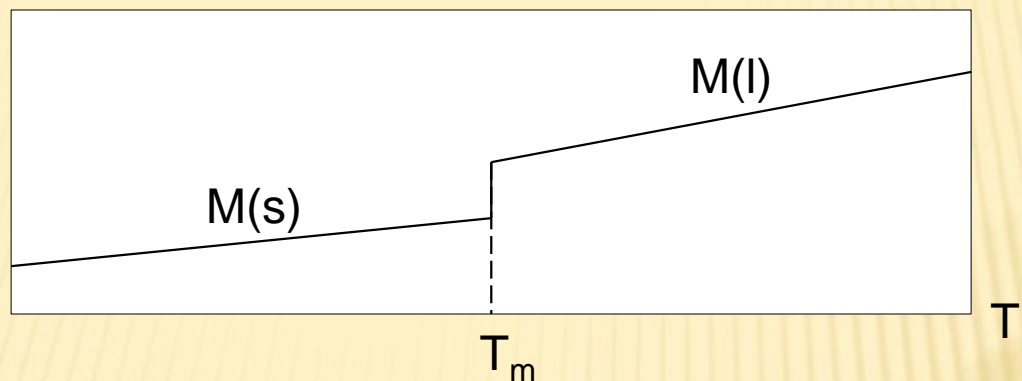
Lines on Ellingham diagrams often have sharp breaks in them which are caused by phase transformations

The straight line representation of ΔG° vs T relationships are valid if there is no physical change taking place for any one of the components taking part in the reaction equilibrium

Consider the transformation of M(s) to M(l) at T_m

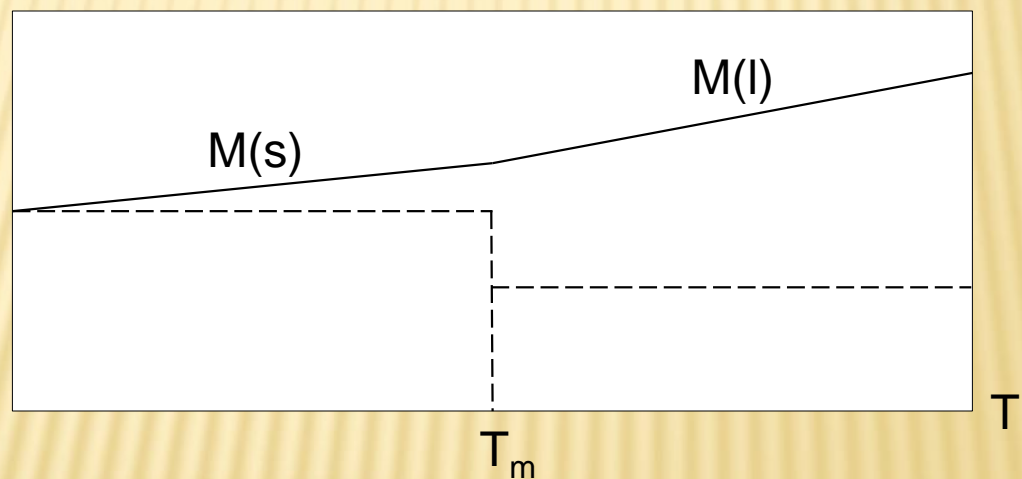


$$-T\Delta S^\circ$$

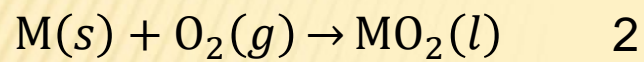
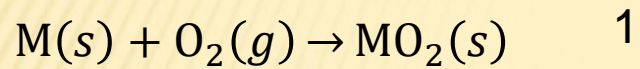


The net effect of phase transformation of a reactant from a low temperature to a high temperature phase is an increase in slope

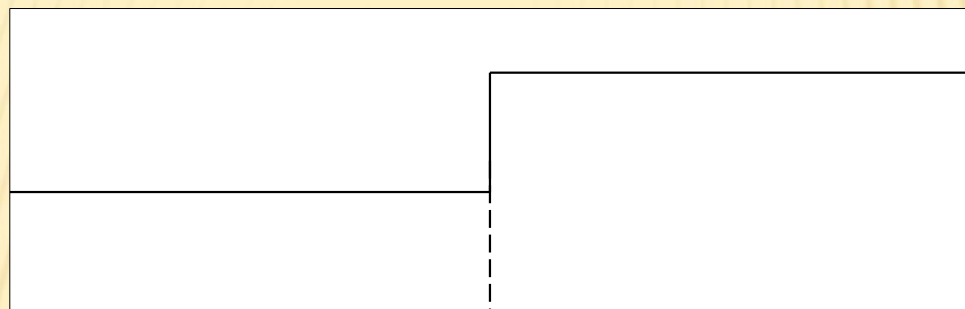
$$\Delta G^\circ$$



Consider the transformation of product $\text{MO}_2(\text{s})$ to $\text{MO}_2(\text{l})$ at T_m



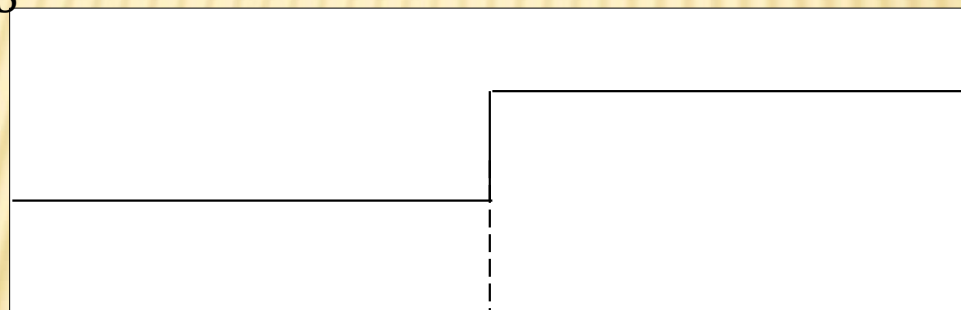
ΔH°



T

T_m

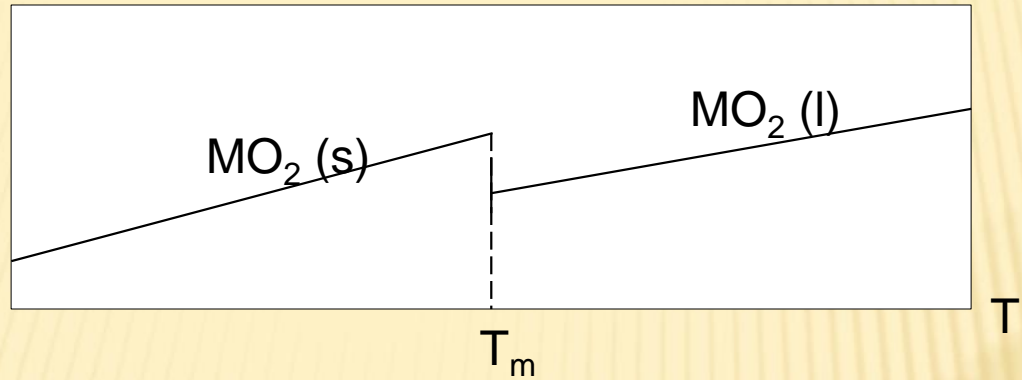
ΔS°



T

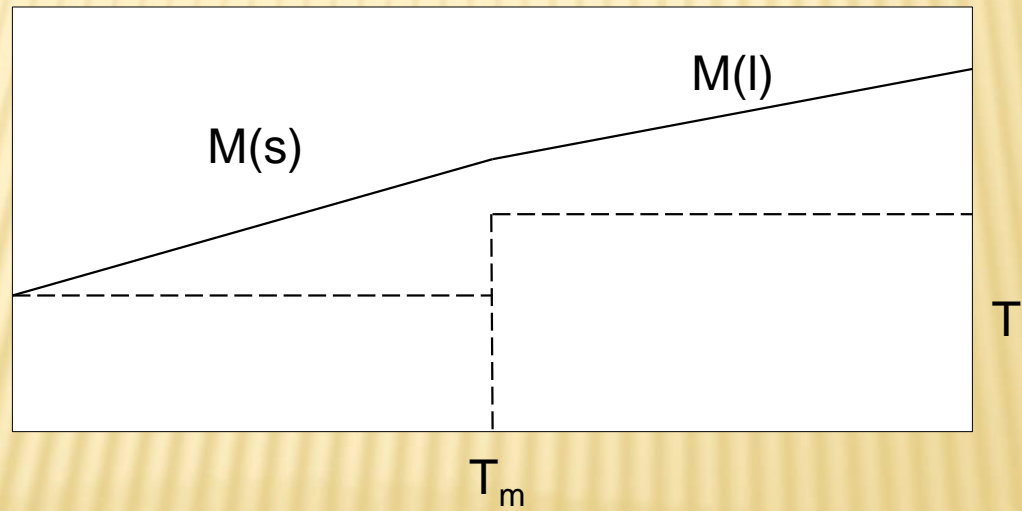
T_m

$$-T\Delta S^\circ$$

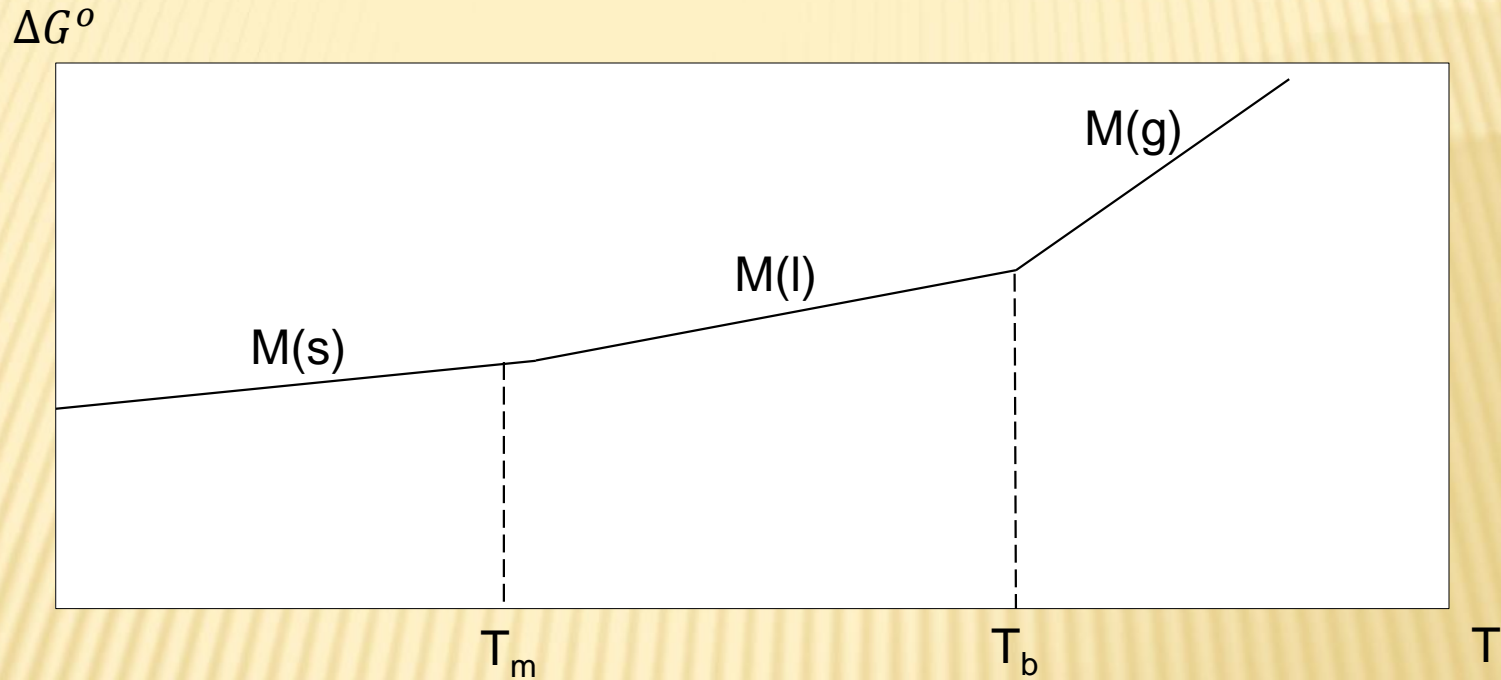


The net effect of phase transformation of a product from a low temperature to a high temperature phase is a decrease in slope

$$\Delta G^\circ$$

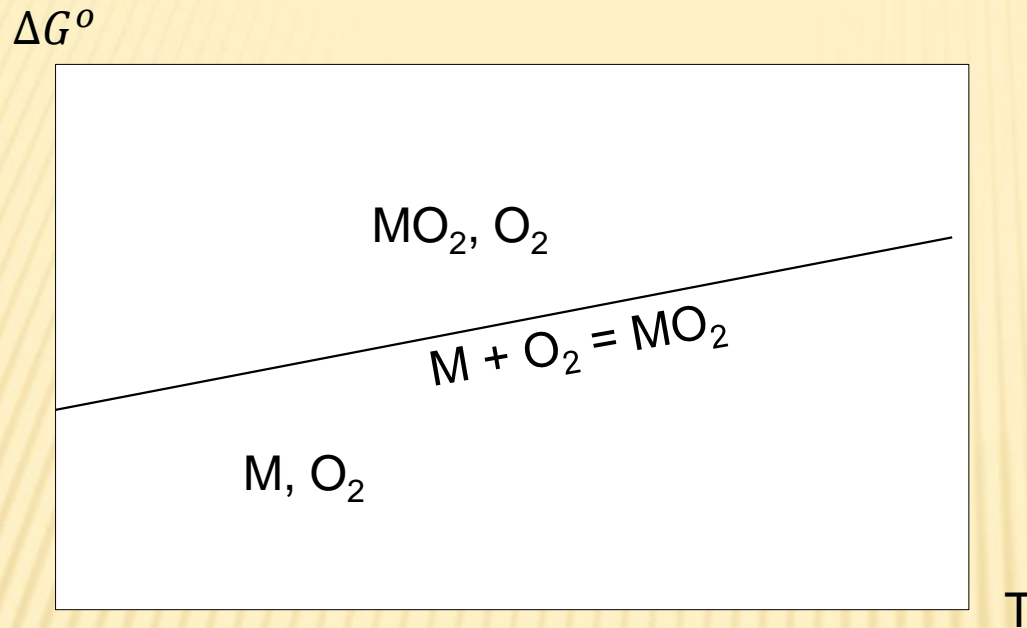


Effect of evaporation on ΔG° vs T plots is similar to melting, but more pronounced since ΔH°_v is about 10 times greater than ΔH°_m



Slope changes for allotropic transformations will be less than that for melting

The Ellingham line for the M/MO₂ equilibrium is shown in the figure



$\Delta G = 0$ all along the line and oxygen partial pressure is $P_{O_2}(eqm)$

Let the partial pressure of oxygen be $P_{O_2}(actual)$ when a metal is exposed to an oxidizing atmosphere

$$\Delta G = \Delta G^\circ + RT \ln \frac{1}{P_{O_2}(actual)}, \quad \Delta G = RT \ln P_{O_2}(eqm) - RT \ln P_{O_2}(actual)$$

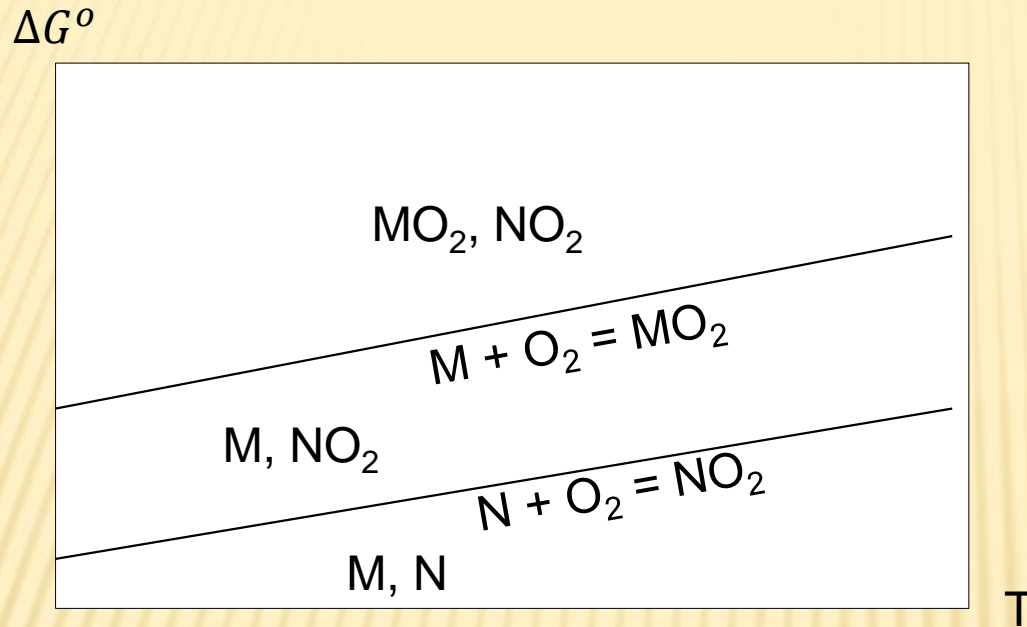
At any point above the line, $P_{O_2}(actual) > P_{O_2}(eqm)$, then $\Delta G < 0$

This implies that MO₂ formation is spontaneous and MO₂ is stable above the line

At any point below the line, $P_{O_2}(actual) < P_{O_2}(eqm)$, then $\Delta G > 0$

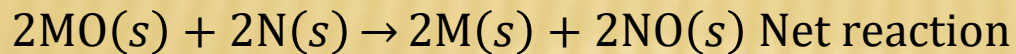
This implies that MO₂ formation is impossible and M is stable below the line

Most of the lines on Ellingham diagram are almost parallel to each other
 Consider the Ellingham lines for the M/MO₂ and N/NO₂ equilibria:

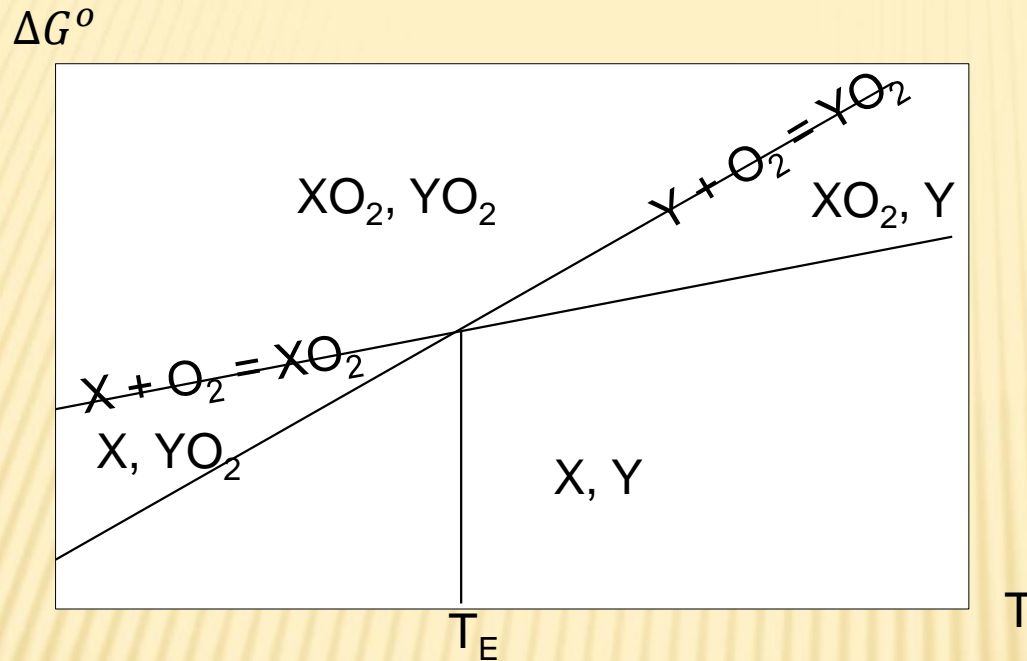


The oxide with the larger region of stability is more stable
 It is evident from the figure that NO is relatively more stable than MO

The element with the more stable oxide is more reactive
 The element of the less stable oxide is more stable in elemental form, M is more stable than N



Ellingham lines sometimes intercept each other
 Consider the two lines for X/XO and Y/YO equilibria:



Relative stability of oxides changes with temperature in this case

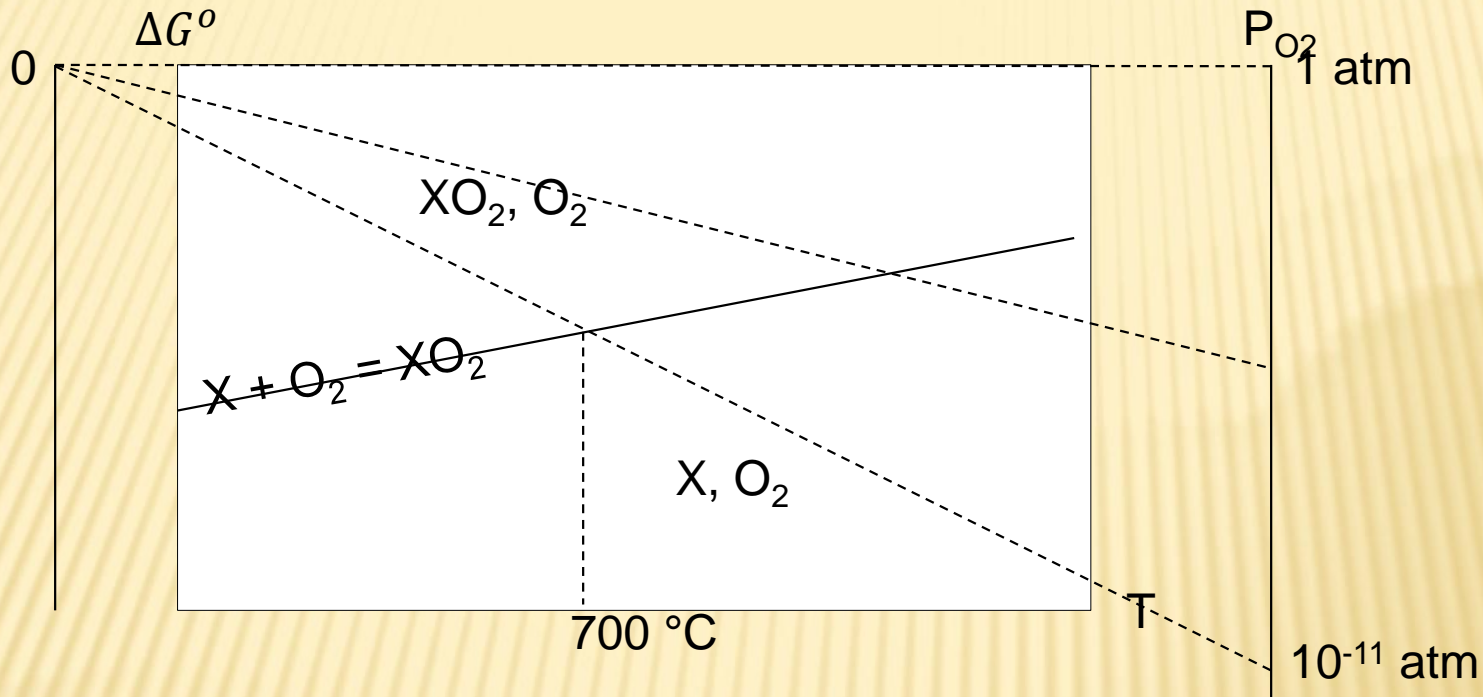
Below the equilibrium temperature, YO_2 is more stable, XO_2 becomes more stable above T_E

All the components X, Y, XO_2, YO_2 coexist at the equilibrium temperature

There is no stability region for Y and XO_2 together below T_E , and for X, YO_2 together above T_E

If Y and XO_2 are brought together at a temperature below T_E , Y will be oxidized while XO_2 will be reduced

Partial pressure grid lines



Ellingham diagram offers a simple and useful way to estimate equilibrium oxygen pressures as a function of temperature

For constant P_{O_2} values, ΔG° vs T is represented by straight lines with $R \ln P_{O_2}$ slope and $\Delta G^\circ = 0$ intercept

Constant oxygen partial pressures can be read from the oxygen partial pressure scale when these lines are superimposed

The intersections of the constant oxygen partial pressure lines and the X- XO_2 equilibrium line give the equilibrium oxygen partial pressures for this reaction at various temperatures

Oxygen partial pressure at $700 \text{ }^\circ\text{C}$, in equilibrium with X and XO_2 is 10^{-11} atm

Oxide is stable if the oxide lines are under the partial pressure line at a temperature

Practice Questions

1. What are the most and least stable metals at room temperature according to the Ellingham diagram?
2. What are the most and least stable oxides at 1400 C according to the Ellingham diagram?
3. Why are the slopes of many of the lines on the Ellingham diagram almost identical? What are the exceptions?
4. What is the best reducing element at very high temperature (>2000 C)?
5. Which metal oxides can CO reduce at all temperatures?
6. What is the oxygen partial pressure that is in equilibrium with Ca and CaO at 1500 C?
7. What is the highest oxygen partial pressure that is in equilibrium with Mg at room temperature?
8. What is the lowest CO/CO₂ pressure ratio that is in equilibrium with Ca at 1400 C
9. Which elements can reduce Cr₂O₃ to Cr at 500 C?
10. Which oxides can Al reduce at 1000 C?
11. A smelting furnace is run at 1800 °C and 10⁻¹⁴ atm partial oxygen pressure to reduce Cr₂O₃. Engineer in charge of production wants to reduce the temperature to cut electrical costs. How many degrees should furnace temperature be lowered while keeping oxygen pressure constant?
12. What should the temperature of a furnace to reduce Cu₂O by solid carbon (C + O₂ = 2CO) be set minimally? How does the reaction quotient K for the overall reduction reaction with increasing temperature?
13. Is Mn stable at an oxygen partial pressure of 10⁻²² atm and 800 °C? If not, what should be done to obtain Mn at this condition?
14. Will the reaction
$$2\text{Cu(l)} + \frac{1}{2} \text{O}_2\text{(g)} = \text{Cu}_2\text{O(s)}$$
go spontaneously to the right or to the left at 1500 C when oxygen pressure is 1 atm?
15. At what partial oxygen pressure will above reaction spontaneously go in the other direction?

$\Delta G^\circ = RT \ln p_{O_2}$, kJ

