Contents of Today

Review previous / Quiz

Equlibrium

Thermodynamic activity
Chemical equilibrium
Gaseous equilibrium
Solid-vapor equilibrium
Sources of information on
Chemical equilibrium and adiabatic flame temperature
etc.

Science research is an adventure, is an interest-driving learning process.
It takes more time to think than to do. – Ke Lu

Quiz Question 1

1) Consider an isolated system consisting of a kilogram of lead and a kilogram of water illustrated below.

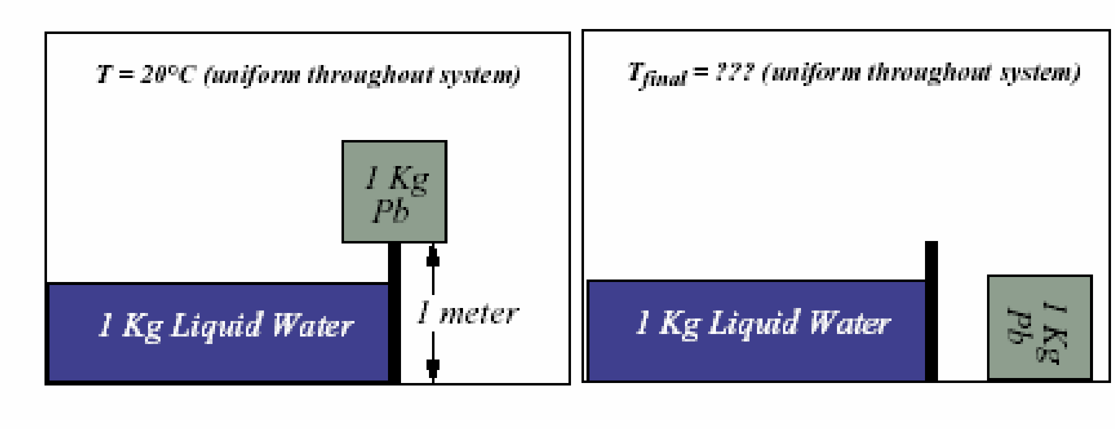


Figure : Isolated system illustrated before and after.

The heat capacity of 1 kilogram of Pb is given by C_{Pb} ; the heat capacity of 1 kilogram of water is given by C_{H2O}; all other heat capacities in the isolated system can be neglected. C_{Pb} and C_{H2O} may be considered independent of any constraints (e.g., constant pressure or constant volume) and to be independent of temperature.

i Derive an expression for the final temperature after a process leading to the figure on the right of the illustration.

ii Would the temperature be larger or smaller if the block of lead had fallen to the left (i.e., into the water)?

Quiz Q1 Answer

1-3-i Derive an expression for the final temperature after a process leading to the figure on the right of the illustration.

Change in internal energy of system =Heat flow into Pb and water

$$|mgh| = C_{\mathrm{Pb}}(T_{final} - 20) + C_{\mathrm{H_2O}}(T_{final} - 20)$$

$$T_{final} = 20 + \frac{|mgh|}{C_{\mathrm{Pb}} + C_{\mathrm{H_2O}}}$$

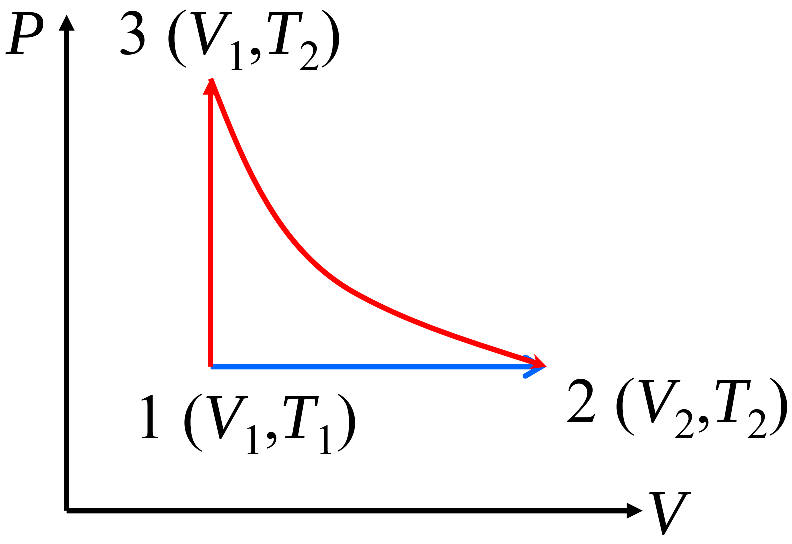
1-3-ii Would the temperature be larger or smaller if the block of lead had fallen to the left (i.e., into the water)?

Tricky. The answer is that the temperature will be lower.

The center of mass of the water will raise and so part of the potential energy of the lead weight will be converted to potential energy of the water. $|mgh|$ would be decreased by an amount corresponding to the raise of center of mass of the water.

Quiz Question 2

2) 1mol 理想气体等压膨胀到状态2，求Q,W,ΔU,ΔH。若将理想气体先等容加热到状态3，然后再等温（可逆）膨胀到状态2，求Q,W,ΔU,ΔH，并与直接从1到2的途径相比较。



Quiz Q2 Answer

1mol 理想气体等压膨胀到状态2，求Q,W,ΔU,ΔH。若将理想气体先等容加热到状态3，然后再等温（可逆）膨胀到状态2，求Q,W,ΔU,ΔH，并与直接从1到2的途径相比较。

1 mol 理想气体直接从1到2等压膨胀

功：$-P_{\text{外}}\times(V_2-V_1)=-R\,(T_2-T_1)$

焓变：$C_p\times(T_2-T_1)$

内能变化：$C_V\times(T_2-T_1)$

热：$Q=\Delta U-W=C_V\times(T_2-T_1)+R\,(T_2-T_1)=C_p\times(T_2-T_1)$

1 mol 理想气体从1到3等容加热

功：W1＝0

焓变：$\Delta H1=C_p\times(T_2-T_1)$

内能变化：$\Delta U1=C_V\times(T_2-T_1)$

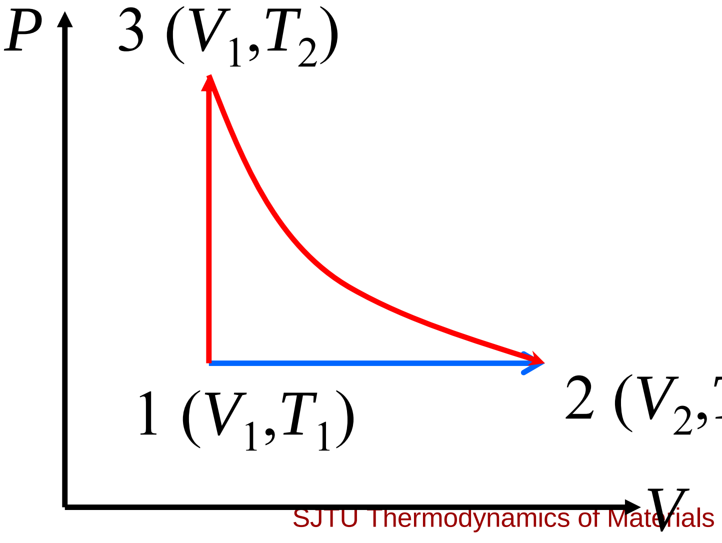
热：$Q1=\Delta U-W=C_V\times(T_2-T_1)$

1 mol 理想气体从3到2（可逆）等温膨胀

$\Delta U2=0,\ \Delta H2=0$　　　$P_{\text{外}}dV=PdV$

$Q2=\Delta U2-W2$

$$W2=-\int_{V1}^{V2}p\,dV=-\int_{V1}^{V2}\frac{RT_2}{V}\,dV=-RT_2\ln\frac{V_2}{V_1}$$



15. 进行下述过程时，系统的 ΔU、ΔH、ΔS 和 ΔG 何者为零？

(1) 非理想气体的卡诺循环；

(2) 隔离系统中的任意过程；

(3) 在 100℃，101325Pa 下 1mol 水蒸发成水蒸气；

(4) 绝热可逆过程。

16. 改正下列错误：

(1) 在一可逆过程中熵值不变；

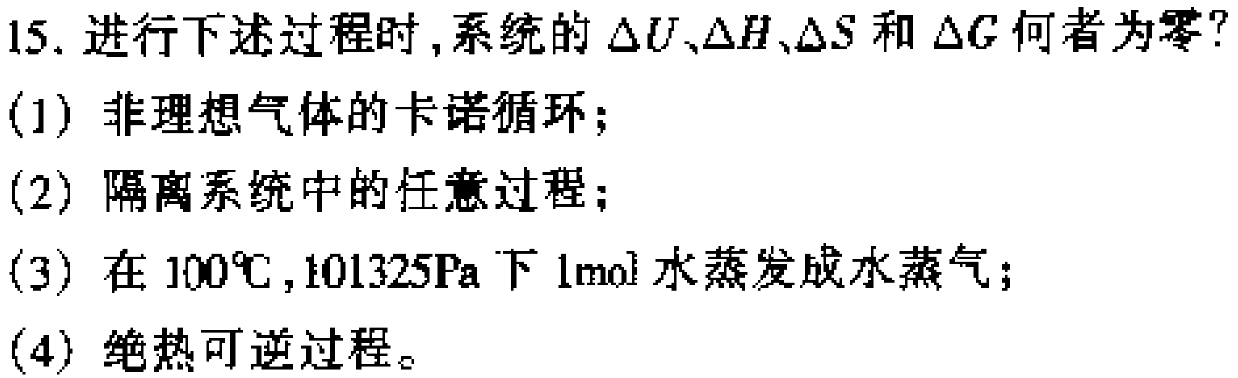
(2) 在一过程中熵变是 $\int \frac{\delta Q}{T}$；

(3) 亥姆赫兹函数是系统能做非体积功的能量；

(4) 吉布斯函数 G 是系统能做非体积功的能量；

(5) 焓 H 是系统能以热的方式交换的能量。

Quiz Q3 Answer



15. 进行下述过程时，系统的 ΔU、ΔH、ΔS 和 ΔG 何者为零？

(1) 非理想气体的卡诺循环；

(2) 隔离系统中的任意过程；

(3) 在 100℃，101325Pa 下 1mol 水蒸发成水蒸气；

(4) 绝热可逆过程。

15题：1）内能变化为0，焓变为0，熵变为0，自由能变化为0。

2）：内能变化为0，焓变不一定为0，熵变不一定为0，自由能变化不一定为0。

3）自由能变化为0。错，主要认为相变过程中内能为0，焓变也为0。

4）只有熵变为0。错误很多。

Review previous lecture (1)

Condition of equilibrium
Phase equilibrium相平衡/化学反应的平衡

$$\delta W_{rev.1\rightarrow 2} = 0$$

$$\mu_{i,2} = \mu_{i,1} \qquad \overline{G}_{i,2} = \overline{G}_{i,1}$$

恒温下 $(\partial \Delta G/\partial P)_T = \Delta V$ 关系式的应用

在298K和1atm下，石墨为稳定态　　298K　石墨(G) -> 金刚石(D)

已知：石墨和金刚石的标准生产热和标准熵为

0，1900 $J.mol^{-1}$，　5.73 $J.mol^{-1}.K^{-1}$, 2.43 $J.mol^{-1}.K^{-1}$

298K下石墨和金刚石密度为：2.22 $g.cm^{-3}$, 3.515 $g.cm^{-3}$

$$V_D = 12/3.515 = 3.414\ cm^3 \cdot mol^{-1}$$

$$V_G = 5.405\ cm^3 \cdot mol^{-1}$$

$$\Delta_G^D G_m(298K, 1atm) = \Delta H_m - T\Delta S_m$$

$$= 1900 - 298(2.43 - 5.73) = 2883\ J \cdot mol^{-1} > 0$$

$$\boxed{\left(\frac{\partial \Delta G}{\partial p}\right)_T = \Delta V = V_D - V_G < 0}$$

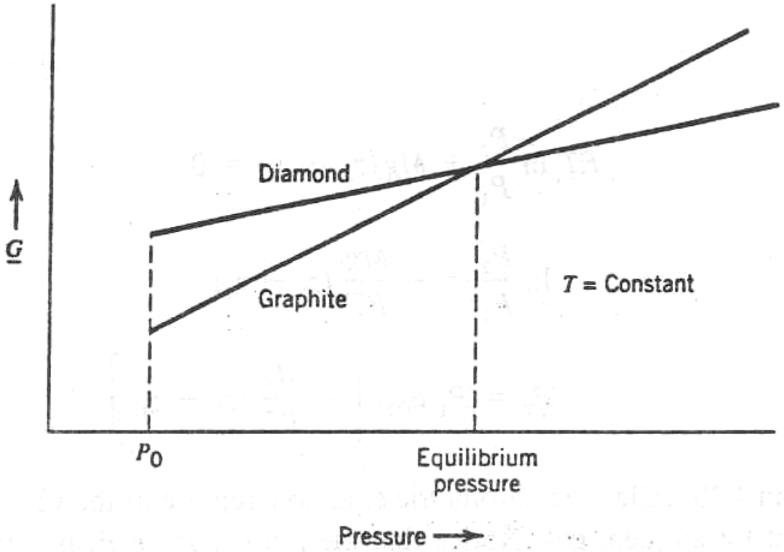


Figure 4.3 Specific Gibbs free energy versus pressure at constant temperature for graphite and diamond.

Review previous lecture (2)

Clapeyron equation in vapor equilibria

Clapeyron equation

$$dp^{eq} \Big/ dT^{eq} = \frac{\Delta \underline{H}}{T^{eq}\Delta \underline{V}}$$

Change of the melting point of tin resulting from a pressure change of 500 atm

$$\Delta p^{eq} \Big/ \Delta T^{eq} = \frac{\Delta \underline{H}}{T^{eq}\Delta \underline{V}} = \frac{7196}{505 \times 4.39 \times 10^{-7}}$$

$$\Delta p^{eq} = 500 atm \quad \Delta T^{eq} = +1.58K$$

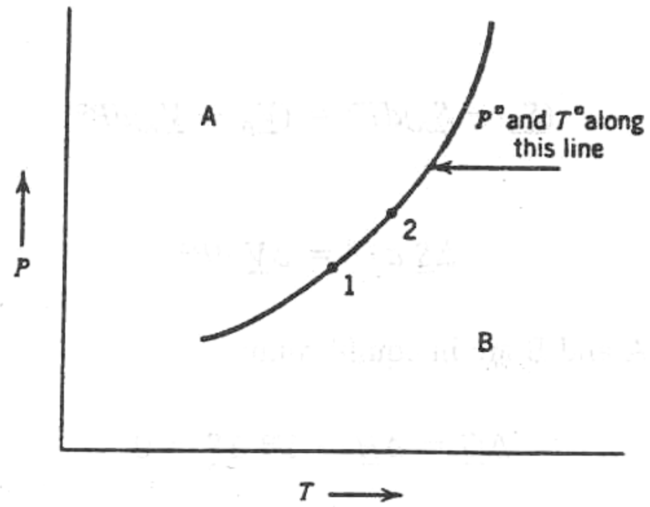


Figure 4.4 Pressure–temperature relationship for equilibrium between phases A and B.

Variation of vapor pressure with particle size

The pressure on a small droplet is the sum of the imposed gas pressure and the internal pressure generated by the surface tension of the material

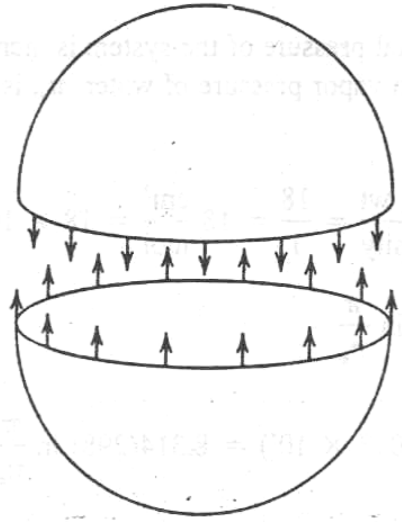


Figure 4.7 The force holding two hemispheres together is $2\pi r\gamma$; the force pushing them apart is $\pi r^2 \Delta P$, where $\Delta P = 2\gamma/r$.

$$2\pi r\gamma = \pi r^2 \Delta p$$

$$\Delta p = \frac{2\gamma}{r}$$

$$\underline{V}_l p_T = RT \ln \frac{\pi}{\pi_e}$$

$$\underline{V}_l \left(\frac{2\gamma}{r} \right) = RT \ln \frac{\pi}{\pi_e}$$

$$\ln \frac{\pi}{\pi_e} = \frac{\underline{V}_l}{RT} \left(\frac{2\gamma}{r} \right)$$

The vapor pressure above the small particles is greater than the vapor pressure above the large particles. Material would then move through the gas phase from small particles to larger ones. Coarsening

Second-order transition

First derivatives of G with respect to T and p are continuous and the second derivatives of G with respect to T and P are discontinuous

$$\underline{S}_A = \underline{S}_B$$

$$\underline{S} = \underline{S}(T, p)$$

$$d\underline{S} = \left(\frac{\partial \underline{S}}{\partial T}\right)_p dT + \left(\frac{\partial \underline{S}}{\partial p}\right)_T dp$$

$$C_p = T\left(\frac{\partial \underline{S}}{\partial T}\right)_p$$

$$d\underline{S} = \frac{C_p}{T} dT - \left(\frac{\partial \underline{V}}{\partial T}\right)_p dp$$

Second-order transition (2)

$$d\underline{S} = \frac{C_p}{T} dT - \left(\frac{\partial \underline{V}}{\partial T}\right)_p dp$$

$$d\underline{S}_A = d\underline{S}_B$$

$$d\underline{S}_A - d\underline{S}_B = 0 = \frac{C_{p,B} - C_{p,A}}{T^{eq}} dT^{eq} - \left(\underline{V}_B \alpha_B - \underline{V}_A \alpha_A\right) dp^{eq}$$

$$\underline{V}_A = \underline{V}_B = \underline{V}$$

$$\frac{dp^{eq}}{dT^{eq}} = \frac{\Delta C_p}{\underline{V} T^{eq} \Delta\alpha}$$

The thermal expansion coefficient does change!

$$\frac{dp^{eq}}{dT^{eq}} = \frac{\Delta\alpha}{\Delta\beta}$$

Superconductivity: an example

$$C_n - C_s = -VT_c\mu_0\left(\frac{\partial H}{dT}\right)^2_{atT=T_C} \neq 0$$

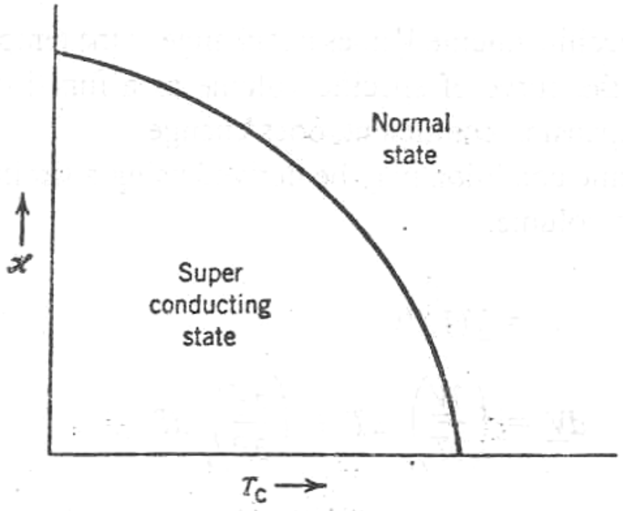


Figure 4.8 Critical temperature as a function of magnetic field for a superconducting material.

Index of nomenclature

Activity：活度

Fugacity：逸度

Reference state / standard state：参考态 / 标准态

Equilibrium constant：平衡常数

Ellingham diagrams：Ellingham图

Introduction

Physical equilibrium.

Chemical equilibrium.

Activity

Fugacity

$$dG = VdP(dG = -SdT + VdP, withdT = 0)$$

$$d\underline{G} = RT\frac{dP}{P} = RTd\ln P$$

5.1 THERMODYNAMIC ACTIVITY (1)

$$dG = VdP(dG = -SdT + VdP, with \quad dT = 0)$$

If the gas is ideal $(\underline{V} = RT/P)$ then :

$$d\underline{G} = RT\frac{dP}{P} = RTd\ln P$$

For a real gas , we can define a function , fugacity (f) ,by analogy to pressure :

$$\boxed{d\underline{G} = RTd\ln f} \qquad Lim f/P = 1 \qquad P \rightarrow 0$$

$$\Delta\overline{G} = \overline{G}_2 - \overline{G}_1 = RT\int_{f_1}^{f_2} d\ln f = RT\ln\frac{f_2}{f_1}$$

$$\boxed{\mu_2 - \mu_1 = RT\ln\frac{f_2}{f_1}}$$

5.1 THERMODYNAMIC ACTIVITY (2)

$$\boxed{\alpha_i \equiv \frac{f_i}{f_i^\circ}}$$

No Units
Reference state: temperature, pressure and physical form
Standard state: pressure and physical form

Gas: pure gas at one atmosphere
Condensed mater: pure liquid or solid under one atmosphere

$$\int_{\underline{G}^\circ}^{\overline{G}} dG_i = \overline{G}_i - \underline{G}_i^\circ = RT\ln\frac{f_i}{f_i^\circ} = RT\ln\alpha_i$$

$$\int_{\underline{G}^\circ}^{\overline{G}} dG_i = \overline{G}_i - \underline{G}_i^\circ = RT\ln\frac{P_i}{P_i^\circ} = RT\ln\alpha_i$$

Ideal gas

The fugacity of a condensed phase is equal to the fugacity of the vapor in equilibrium with it.

The value of thermodynamic activity changes not only with pressure but also with composition.

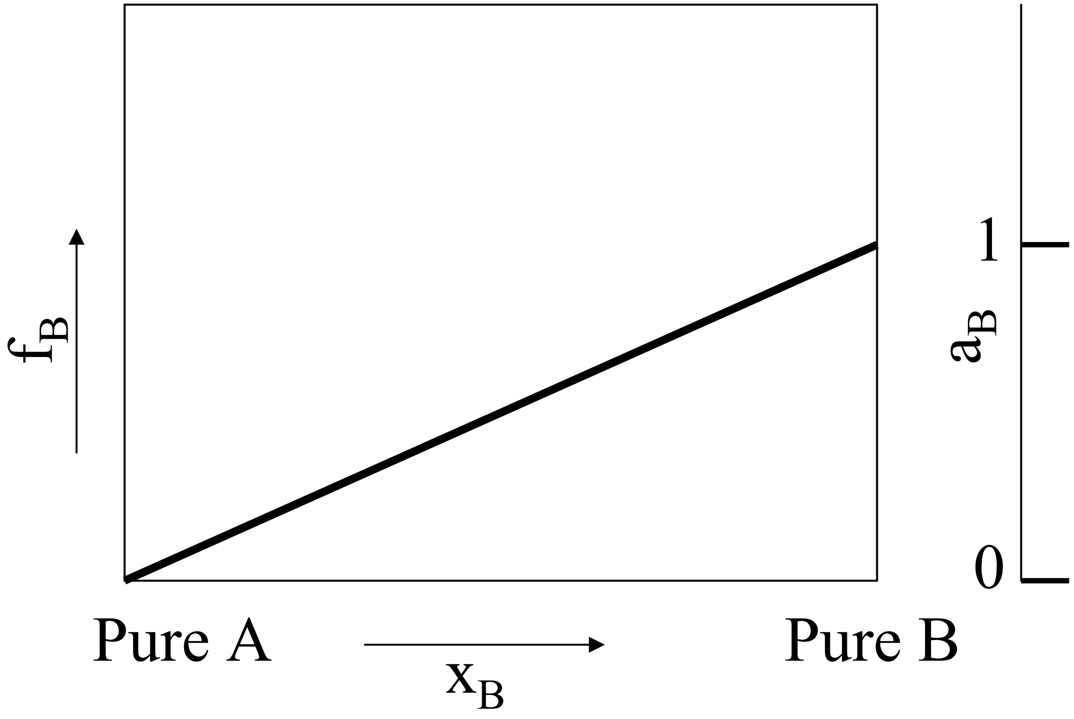
5.1 THERMODYNAMIC ACTIVITY (3)

Pure

$$f_B = x_B f_B^P$$

$$\alpha_B = \frac{f_B}{f_B^\circ} = \frac{x_B f_B^P}{f_B^\circ}$$

Standard state



5.2 CHEMICAL EQUILIBRIUM

$$bB + cC = dD + eE$$

Expression for a chemical reaction

$$\delta W_{rev} = \Delta G = d\overline{G}_D + e\overline{G}_E - b\overline{G}_B - c\overline{G}_C$$

$$\overline{G}_B = \overline{G}_B^\circ + RT\ln\alpha_B$$

$$\Delta G = d(G_D^\circ + RT\ln\alpha_D) + e(G_E^\circ + RT\ln\alpha_E) - b(G_B^\circ + RT\ln\alpha_B) - c(G_C^\circ + RT\ln\alpha_C)$$

$$\Delta G = \Delta G^\circ + RT\ln J_\alpha$$

$$\Delta G^\circ = dG_D^\circ + eG_E^\circ - bG_B^\circ - cG_C^\circ$$

Equilibrium constant

$$J_\alpha = \frac{\alpha_D^d \alpha_E^e}{\alpha_B^b \alpha_C^c}$$

$$\boxed{\Delta G^\circ = -RT\ln J_{\alpha(equilibrium)} = -RT\ln K_\alpha}$$

5.3 GASEOUS EQUILIBRIA

$$\boxed{\frac{1}{2}O_2 \rightarrow O}$$

$$\Delta G^\circ = \Delta G^\circ_{f,0} - \frac{1}{2}\Delta G^\circ_{f,O_2} = 187{,}800 - 0 = 187{,}800J$$

$$\Delta G^\circ = -RT\ln\frac{\alpha_0}{\alpha_{O_2}^{1/2}} = -RT\ln\frac{P_0}{P_{O_2}^{1/2}}$$

$$\ln\frac{P_0}{P_{O_2}^{1/2}} = -\frac{\Delta G^\circ}{RT} = -\frac{187{,}800}{(8.314)(1000)} = -22.58$$

$$\frac{P_0}{P_{O_2}^{1/2}} = 1.5\times10^{-10}$$

Since $P_0 + P_{O_2} = 1atm$ $\quad P_{O_2} = 1 - P_0$

$$P_0 = (1.5\times10^{-10})(1-P_0)^{1/2} \qquad P_0 = 1.5\times10^{-10}$$

5.4 SOLID-VAPOR EQUILIBRIA (1)

$$4Cu(s)+O_2(g)\rightarrow 2Cu_2O(s)$$

T=1000 K

$$\Delta G^\circ = -RT\ln K_\alpha = -RT\ln\frac{\alpha^2_{Cu_2O}}{\alpha^4_{Cu}P_{O_2}}$$

$$\Delta G^\circ = -339{,}000 - 14.24T\ln T + 247T$$

$$\Delta G^\circ = -190{,}360 = 8.314\times 1000\ln P_{O_2}$$

$$\ln P_{O_2} = -22.90,\ P_{O_2} = 1.14\times 10^{-10}\,atm$$

5.4 SOLID-VAPOR EQUILIBRIA (2)

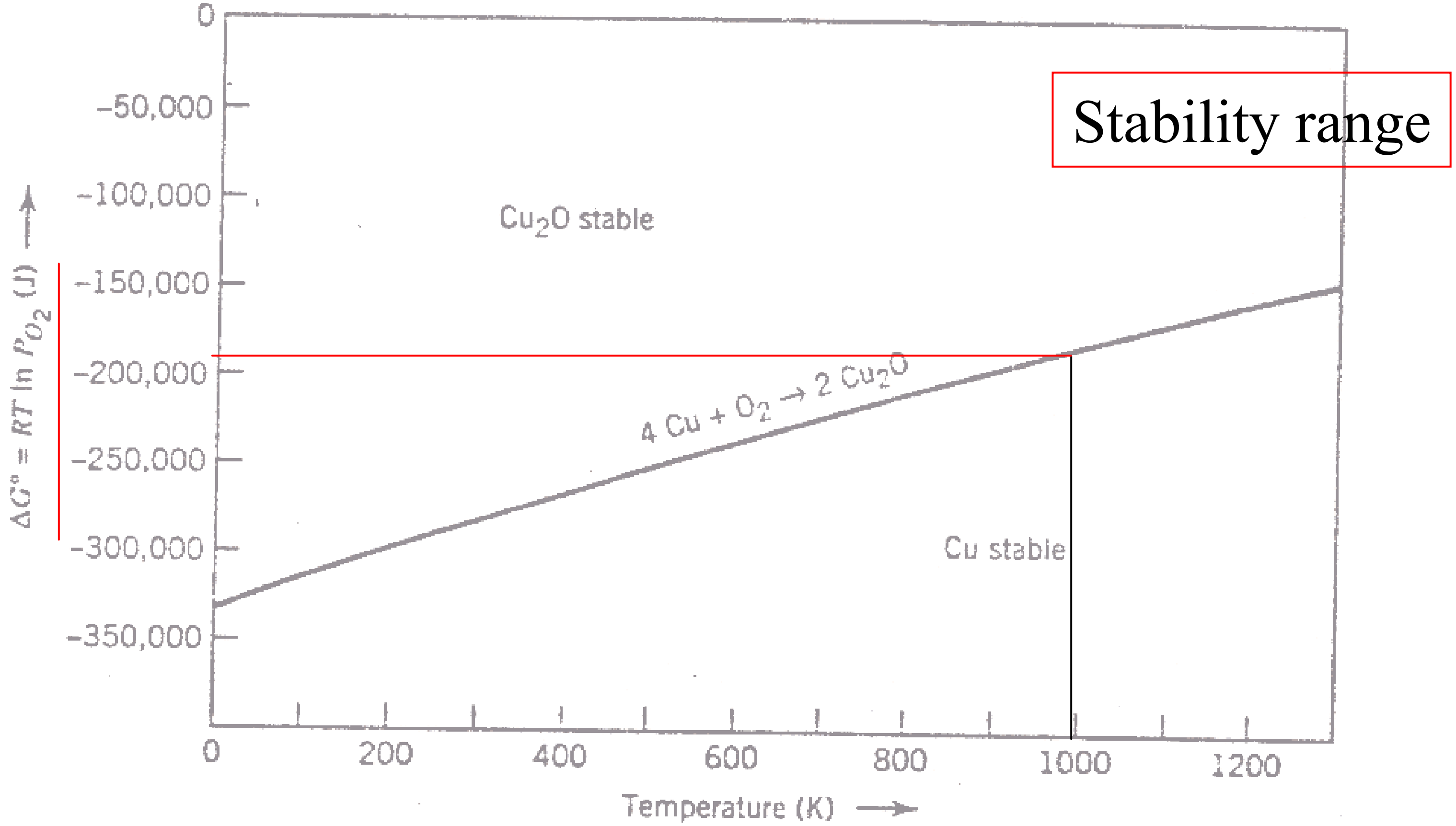


Figure 5.2 ΔG° versus T for the reaction $4Cu + O_2 \rightarrow 2Cu_2O$, showing regions of stability of Cu_2O and Cu.

5.4 SOLID-VAPOR EQUILIBRIA (3)

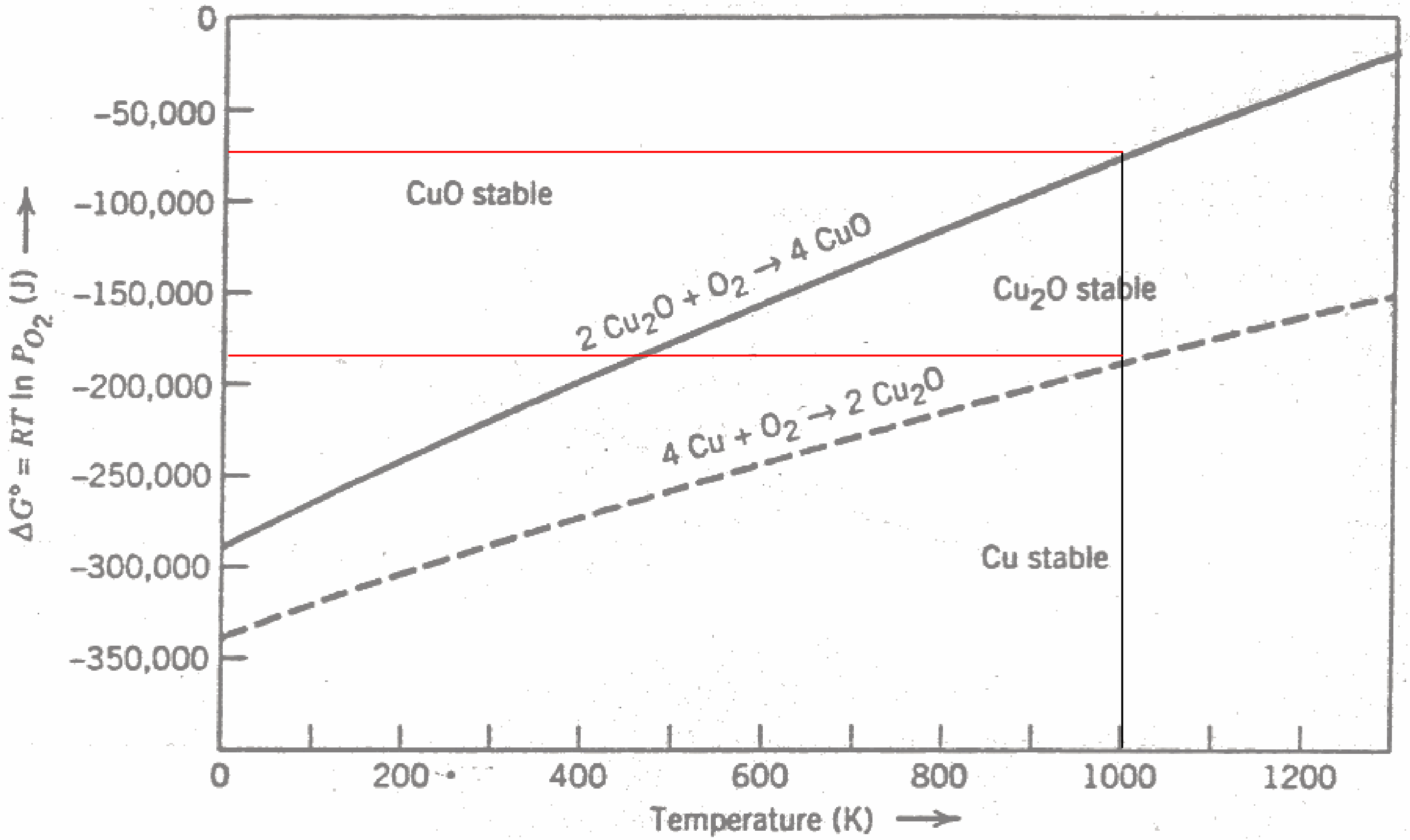


Figure 5.3 ΔG° versus *T* for oxides of copper, showing regions of stability for Cu, Cu_2O, and CuO.

5.5 SOURCES OF INFORMATION ON ΔG° (1)

$$\Delta G_T^{\circ} = \sum_{products} n_p \Delta \underline{G}^{\circ}_{f,T} - \sum_{reactants} n_r \Delta G^{\circ}_{f,T}$$

$$\Delta G_T^{\circ} = \Delta H_T^{\circ} - T \Delta S_T^{\circ}$$

$$\Delta H_T^{\circ} = \Delta H^{\circ}_{298,T} + \int_{298}^{T} \Delta C_P^{\circ} dT$$

$$\Delta S_T^{\circ} = \Delta S^{\circ}_{298,T} + \int_{298}^{T} \left(\frac{\Delta C_P^{\circ}}{T}\right) dT$$

$$\Delta G^{\circ}_{f,T} = A + BT + CT \ln T$$

5.5 SOURCES OF INFORMATION ON ΔG° (2)

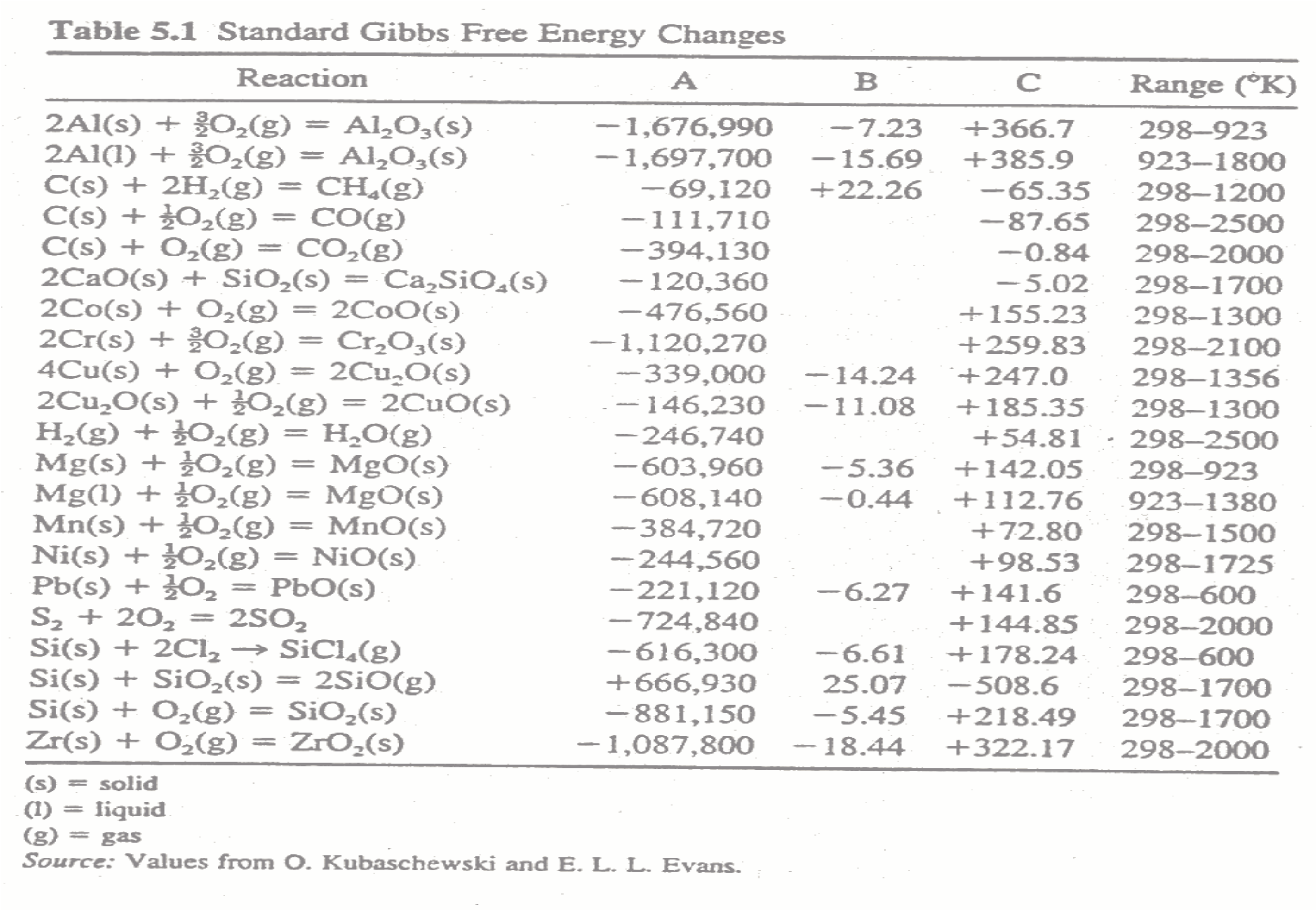


Table 5.1 Standard Gibbs Free Energy Changes

Reaction	A	B	C	Range (°K)
$2Al(s) + \frac{3}{2}O_2(g) = Al_2O_3(s)$	−1,676,990	−7.23	+366.7	298–923
$2Al(l) + \frac{3}{2}O_2(g) = Al_2O_3(s)$	−1,697,700	−15.69	+385.9	923–1800
$C(s) + 2H_2(g) = CH_4(g)$	−69,120	+22.26	−65.35	298–1200
$C(s) + \frac{1}{2}O_2(g) = CO(g)$	−111,710		−87.65	298–2500
$C(s) + O_2(g) = CO_2(g)$	−394,130		−0.84	298–2000
$2CaO(s) + SiO_2(s) = Ca_2SiO_4(s)$	−120,360		−5.02	298–1700
$2Co(s) + O_2(g) = 2CoO(s)$	−476,560		+155.23	298–1300
$2Cr(s) + \frac{3}{2}O_2(g) = Cr_2O_3(s)$	−1,120,270		+259.83	298–2100
$4Cu(s) + O_2(g) = 2Cu_2O(s)$	−339,000	−14.24	+247.0	298–1356
$2Cu_2O(s) + \frac{1}{2}O_2(g) = 2CuO(s)$	−146,230	−11.08	+185.35	298–1300
$H_2(g) + \frac{1}{2}O_2(g) = H_2O(g)$	−246,740		+54.81	298–2500
$Mg(s) + \frac{1}{2}O_2(g) = MgO(s)$	−603,960	−5.36	+142.05	298–923
$Mg(l) + \frac{1}{2}O_2(g) = MgO(s)$	−608,140	−0.44	+112.76	923–1380
$Mn(s) + \frac{1}{2}O_2(g) = MnO(s)$	−384,720		+72.80	298–1500
$Ni(s) + \frac{1}{2}O_2(g) = NiO(s)$	−244,560		+98.53	298–1725
$Pb(s) + \frac{1}{2}O_2 = PbO(s)$	−221,120	−6.27	+141.6	298–600
$S_2 + 2O_2 = 2SO_2$	−724,840		+144.85	298–2000
$Si(s) + 2Cl_2 \rightarrow SiCl_4(g)$	−616,300	−6.61	+178.24	298–600
$Si(s) + SiO_2(s) = 2SiO(g)$	+666,930	25.07	−508.6	298–1700
$Si(s) + O_2(g) = SiO_2(s)$	−881,150	−5.45	+218.49	298–1700
$Zr(s) + O_2(g) = ZrO_2(s)$	−1,087,800	−18.44	+322.17	298–2000

(s) = solid
(l) = liquid
(g) = gas

Source: Values from O. Kubaschewski and E. L. L. Evans.

5.5 SOURCES OF INFORMATION ON ΔG°

$$\Delta H_T^\circ = \Delta H_{298}^\circ + \Delta C_P^\circ (T - 298)$$

$$\Delta S_T^\circ = \Delta S_{298}^\circ + \Delta C_P^\circ \ln(\frac{T}{298})$$

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

The difference in heat capacities between reactants and products is small or if the data upon which the standard free values are not sufficiently precise to justify the inclusion of differences in heat capacity.

5.6 ELLINGHAM DIAGRAMS (1)

$$\Delta \underline{G}^{\circ} = +RT \ln P_{O_2}$$

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$K_{\alpha} = \frac{P_{H_2O}^2}{P_{H_2}^2 P_{O_2}}$$

$$P_{O_2} = \frac{1}{K_{\alpha}} \left(\frac{P_{H_2O}}{P_{H_2}}\right)^2$$

5.6 ELLINGHAM DIAGRAMS (2)

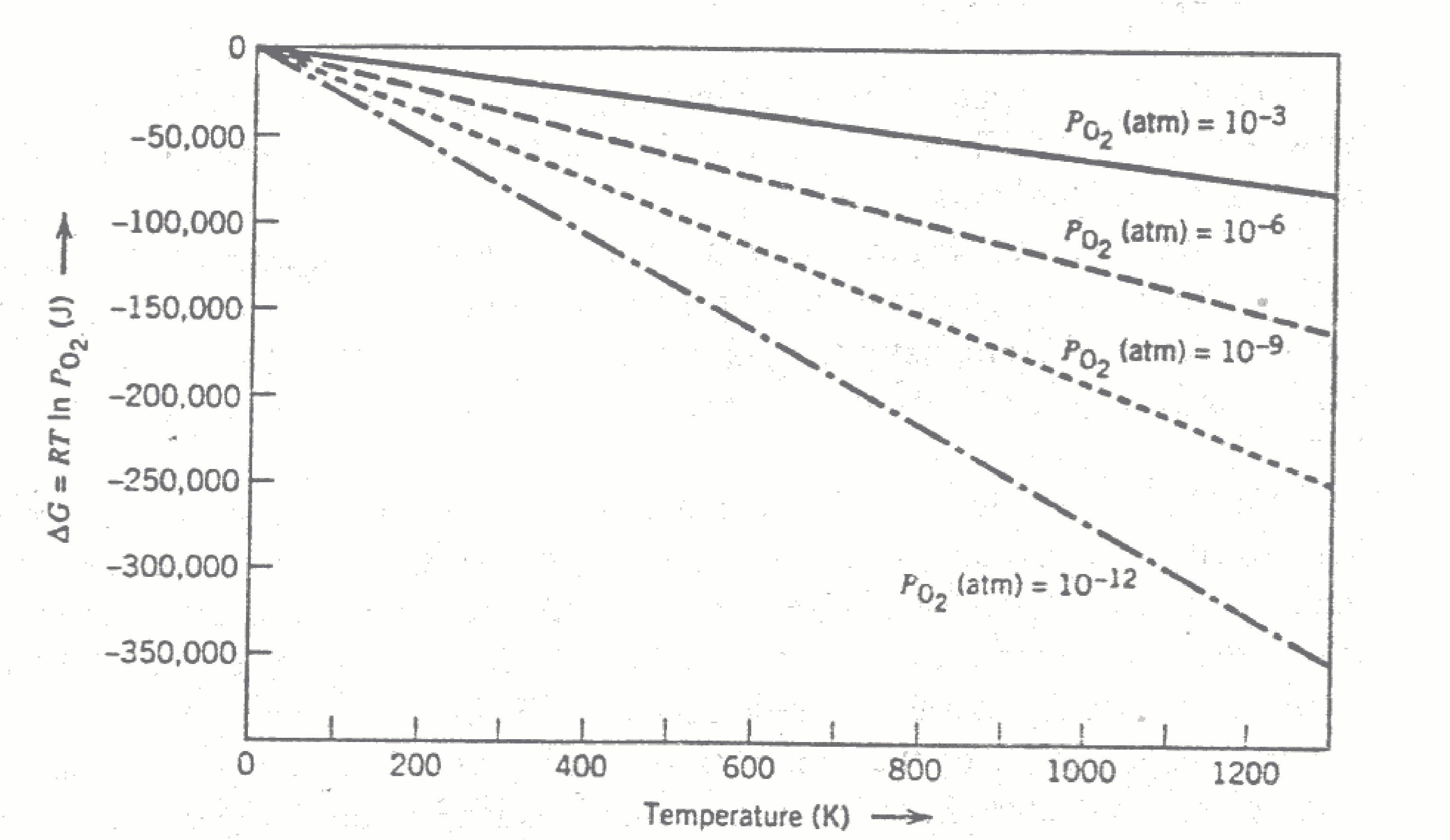


Figure 5.5 Plot of ΔG° versus T, where $\Delta G^\circ = RT \ln P_{O_2}$.

5.6 ELLINGHAM DIAGRAMS (3)

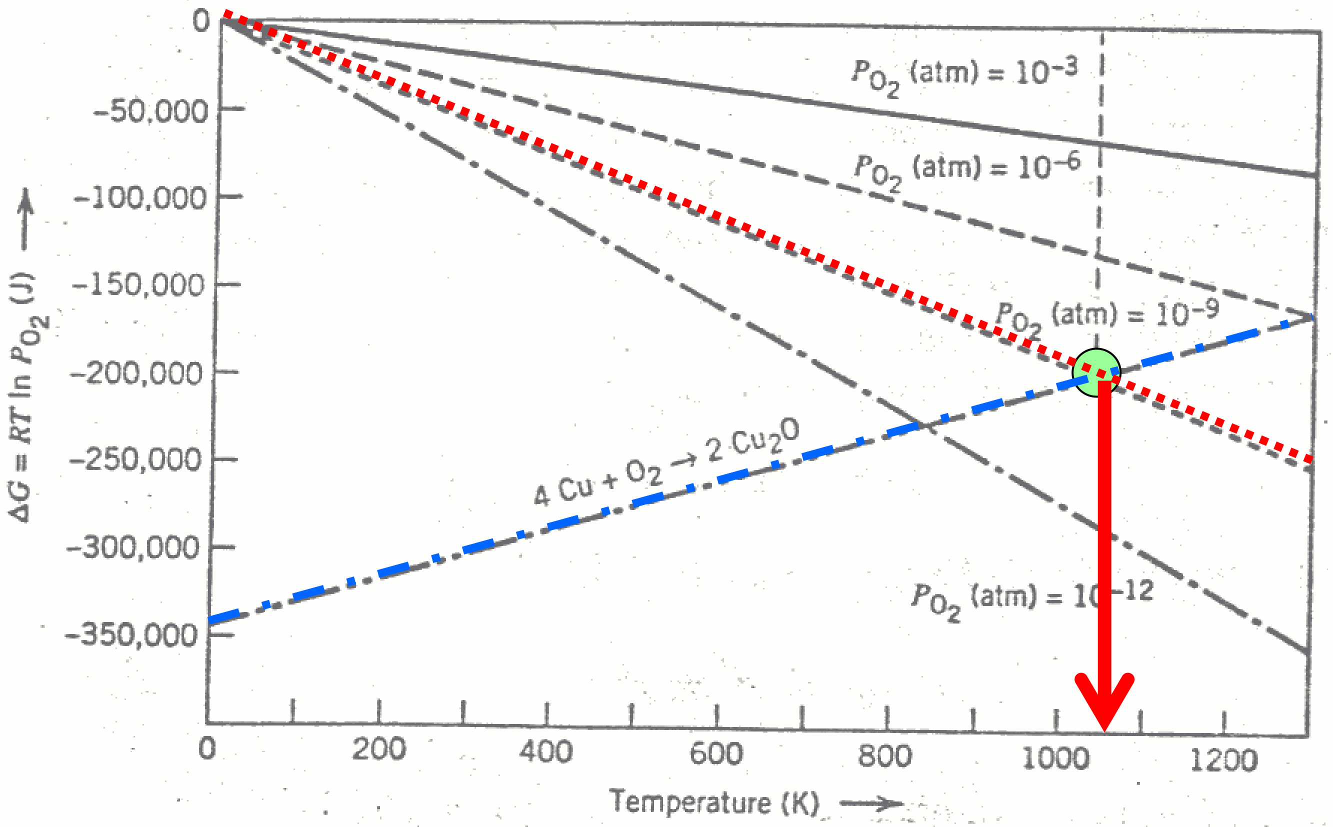


Figure 5.6 Superposition of Figures 5.2 and 5.5. At 1050 K, equilibrium oxygen pressure in the reaction $4Cu + O_2 \rightarrow 2Cu_2O$ is 10^{-9} atm.

1050 K

5.6 ELLINGHAM DIAGRAMS (4)

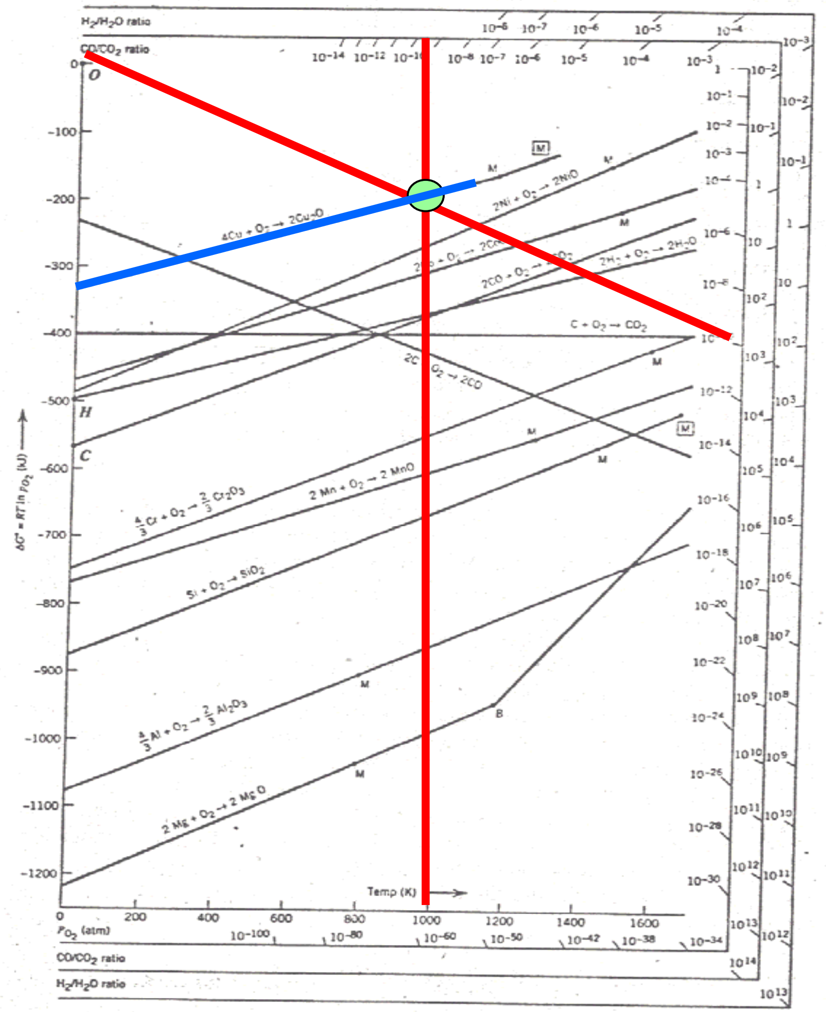


Figure 5.7 Ellingham diagram for some oxides.

Reaction

Temperature

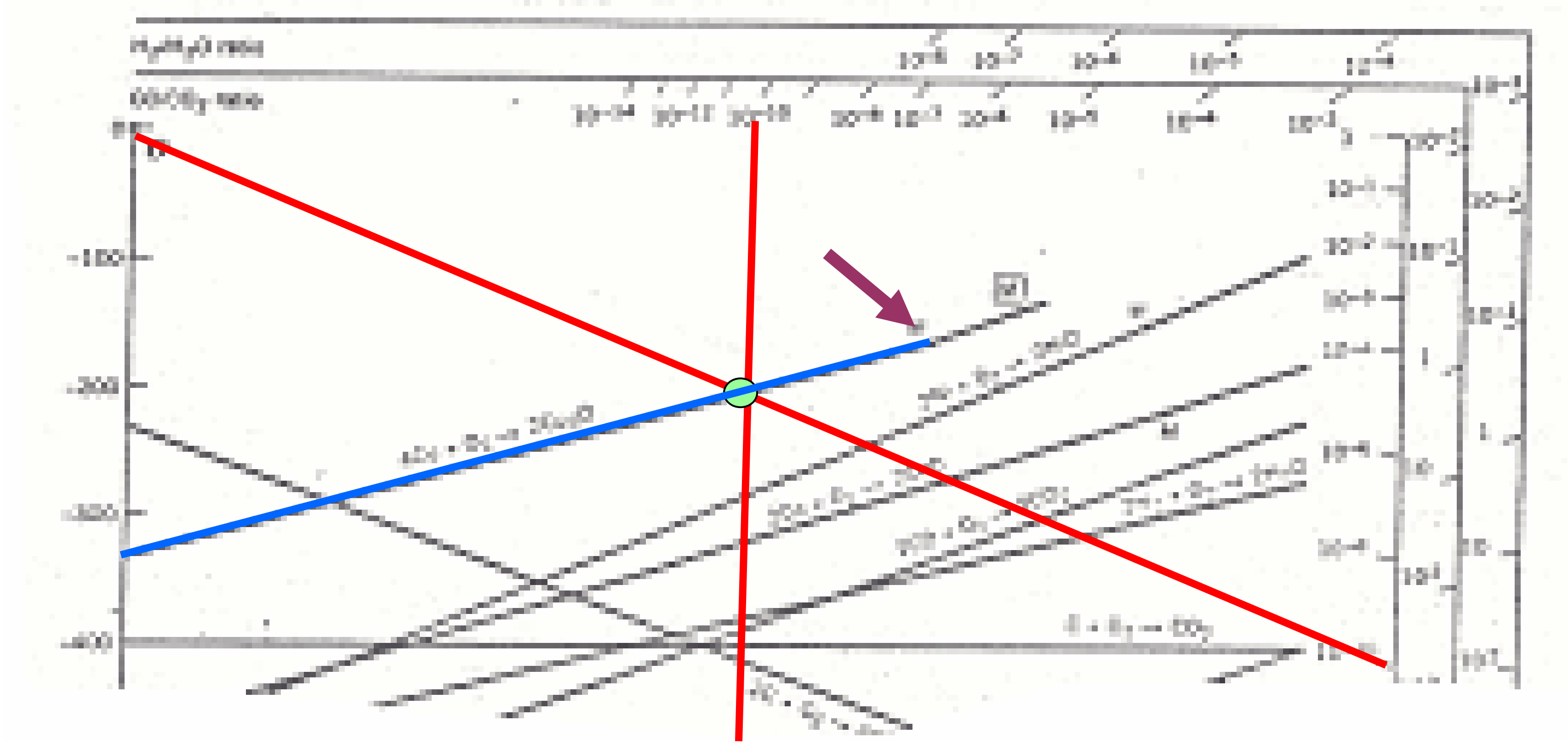
Oxygen pressure

5.6 ELLINGHAM DIAGRAMS (5)

Reaction

Temperature

Oxygen pressure



5.6 ELLINGHAM DIAGRAMS (6)

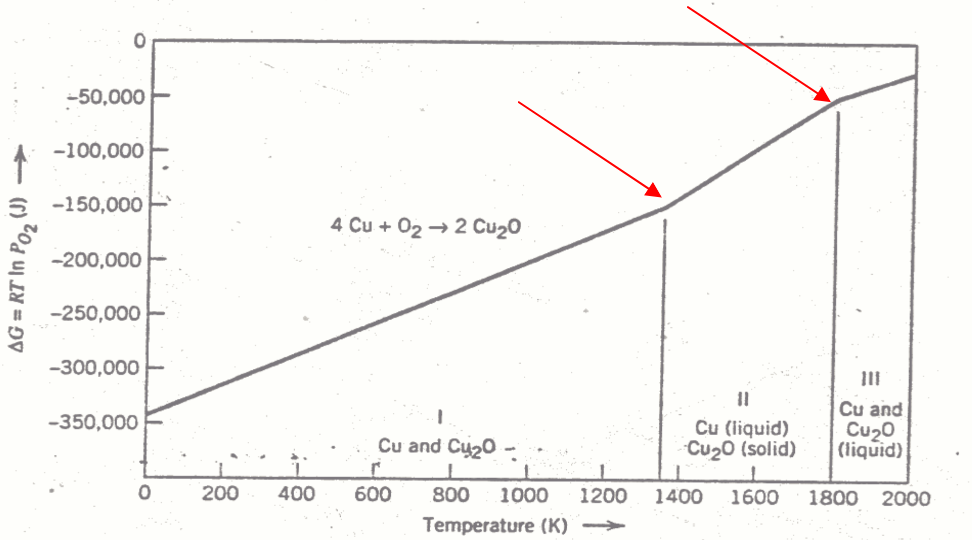


Figure 5.8 Plot of $\Delta G° = RT \ln P_{O_2}$ versus for $4Cu + O_2 \rightarrow 2Cu_2O$, showing change in the slope of the curve at the melting points of condensed phases.

Entropy change
Slope change

$$4Cu(s) + O_2(g) \rightarrow 2Cu_2O(s) \qquad \Delta S^0 = -129.2\ J.mol^{-1}K^{-1}$$

$$4Cu(s) \rightarrow 4Cu(l) \qquad \Delta S^0 = 4 \times 9.7\ J.mol^{-1}K^{-1}$$

$$4Cu(l) + O_2(g) \rightarrow 2Cu_2O(s) \qquad \Delta S^0 = -168\ J.mol^{-1}K^{-1}$$

补充

- 纵轴为指定单质与1摩尔1大气压氧化合成氧化物
- 截距和斜率
- 斜率大多为正，产物为凝聚态，反应物包含气体，熵变减少
- 直线与折线
- 两处例外

$$C(s)+O_2(g)\rightarrow CO_2(g) \qquad \Delta S^0 \approx 0$$

$$2C(s)+O_2(g)\rightarrow 2CO(g) \qquad \Delta S^0 = 42\ J.mol^{-1}K^{-1}$$

5.7 VARIATION OF EQUILIBRIUM CONSTANT WITH TEMPERATURE

$$d(\Delta G^\circ) = -\Delta S^\circ dT \qquad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$d(\Delta G^\circ) = \frac{\Delta G^\circ}{T}dT - \frac{\Delta H^\circ}{T}dT$$

Multiplying by 1/T , we obtain:

$$\frac{d(\Delta G^\circ)}{T} - \frac{\Delta G^\circ}{T^2}dT = -\frac{\Delta H^\circ}{T^2}dT$$

$$d(\frac{\Delta G^\circ}{T}) = d(-R\ln K_\alpha) = \Delta H^\circ d(\frac{1}{T})$$

$$d(\ln K_\alpha) = -\frac{\Delta H^\circ}{R}d(\frac{1}{T})$$

5.7 VARIATION OF EQUILIBRIUM CONSTANT WITH TEMPERATURE

$$\ln\frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

As an example :

Temperature(K)	Pressure(atm)
1030	0.10
921	0.01

$$\ln\left(\frac{0.10}{0.01}\right) = \ln 10 = \frac{\Delta H^\circ (109)}{(8.314)(921)(1030)}$$

$$\Delta H^\circ = +166{,}000J$$

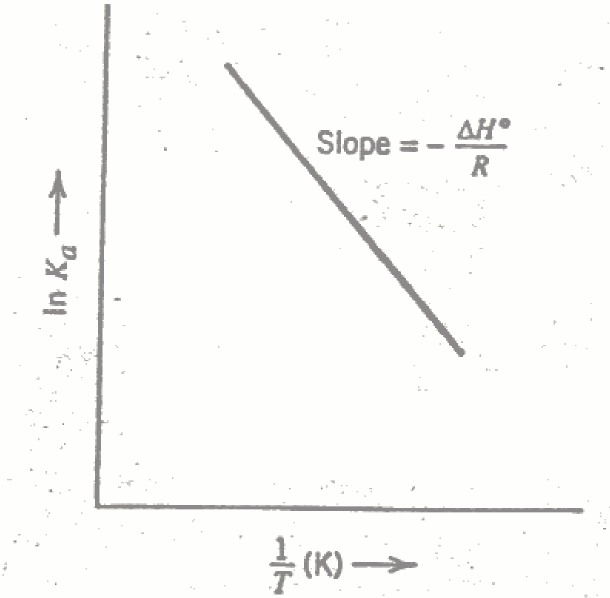


Figure 5.9 Plot of $\ln K_a$ versus $1/T$. For the reaction represented, the slope of the line is $-\Delta H^\circ/R$.

5.8 GASES DISSOLVED IN METALS (SIEVERT'S LAW)

$$H_2(g) = 2H \quad \text{(in copper solution)}$$

$$K_\alpha = \frac{\alpha_H^2}{\alpha_{H_2(g)}}$$

$$\alpha_H = [H]$$

$$K_\alpha = \frac{[H]^2}{P_{H_2}}$$

$$\boxed{[H] = K_\alpha^{1/2} P_{H_2}^{1/2}}$$

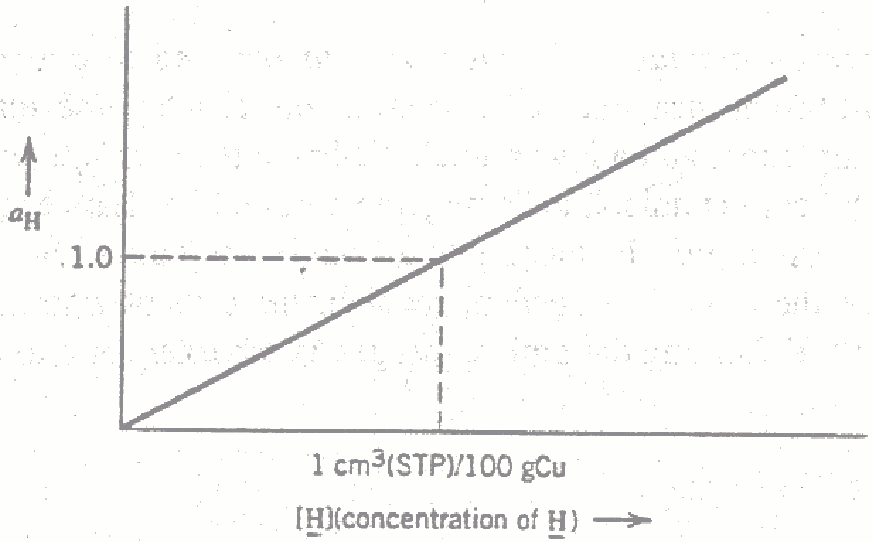


Figure 5.10 Plot of activity of dissolved hydrogen versus concentration.

5.9 CHEMICAL EQUILIBRIUM AND ADLABATIC FLAME TEMPERATURES (1)

Not completion

First law

Chemical equilibrium

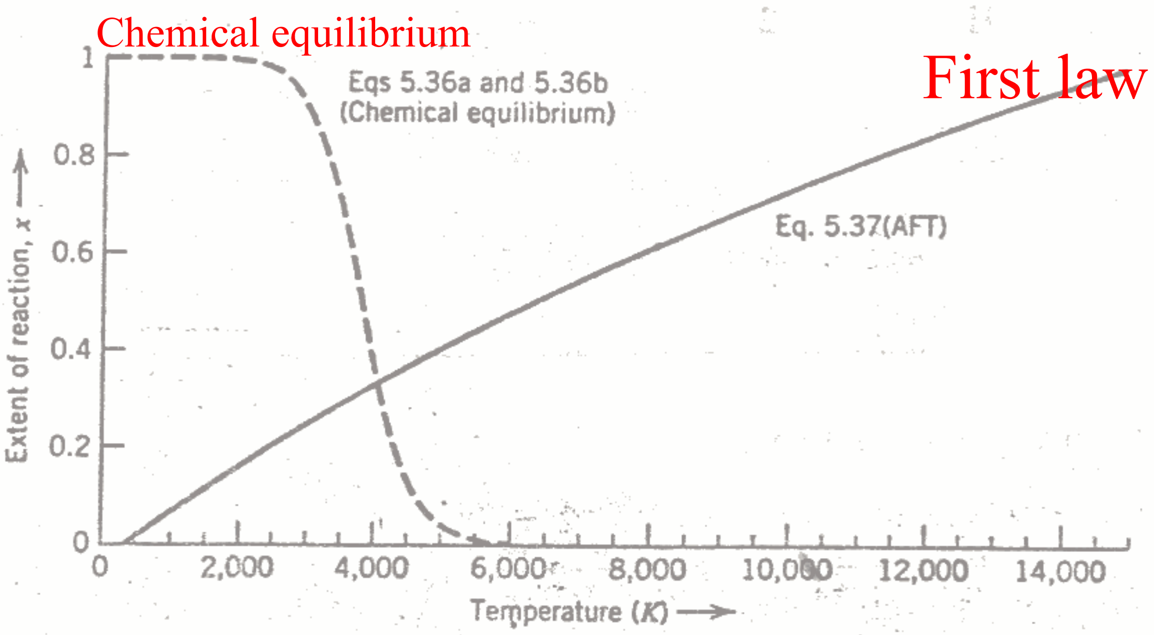


Figure 5.11 The extent of the reaction $2H \rightarrow H_2$ as a function of temperature for the AFT and chemical equilibrium calculations (Eqs. 5.37 and 5.36a, respectively).

Review

Thermodynamic activity
Chemical equilibrium
Gaseous equilibrium
Solid-vapor equilibrium
Sources of information on Gibbs free energy
Chemical equilibrium and adiabatic flame temperature

Homework

- Exercises in Chap 5

  P 144, 5.3, 5.6, 5.15