Chapter 12B

Reactions Involving Pure Condensed Phases and A Gaseous Phase

12. 6 The Oxides of Carbon

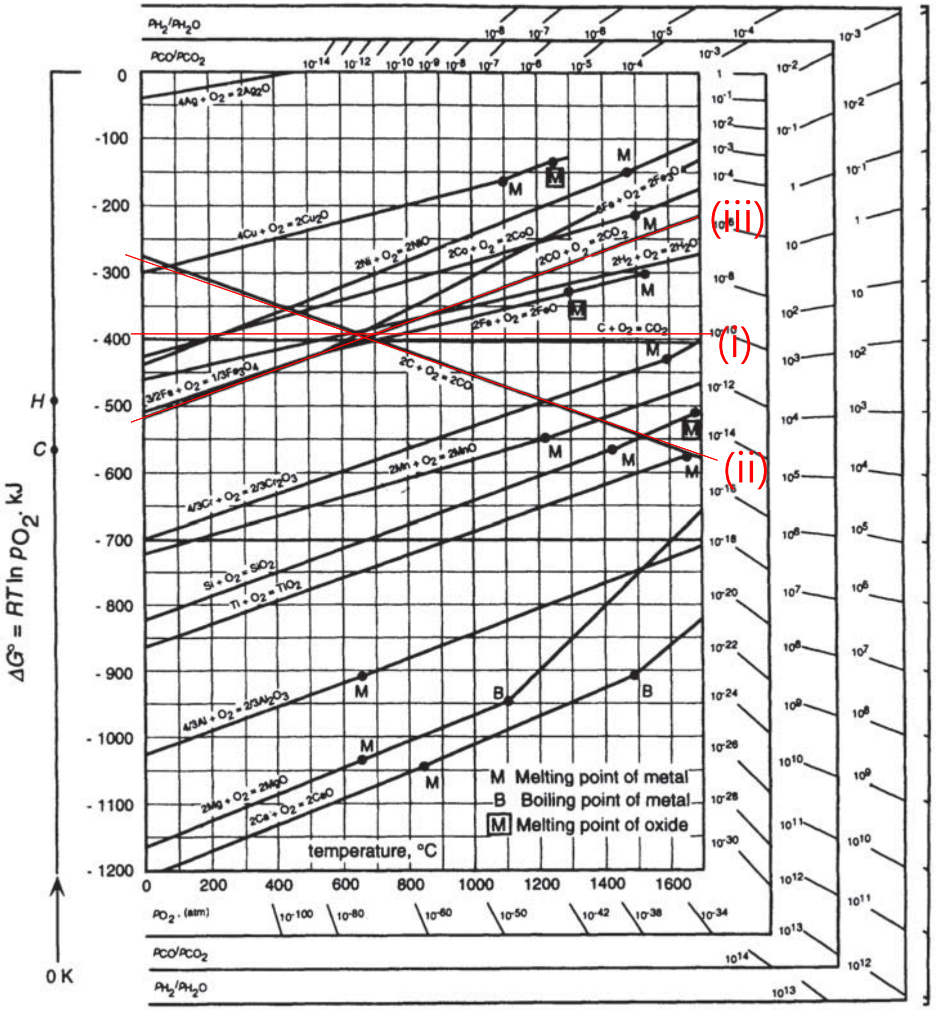


Figure 12.13 The Ellingham diagram for selected oxides.

Carbon forms two gaseous oxides, CO and CO_2, according to

$$C_{(gr)} + O_{2(g)} = CO_{2(g)} \quad \text{(i)} \quad \Delta G^0_{(i)} = -394{,}100 - 0.84TJ$$

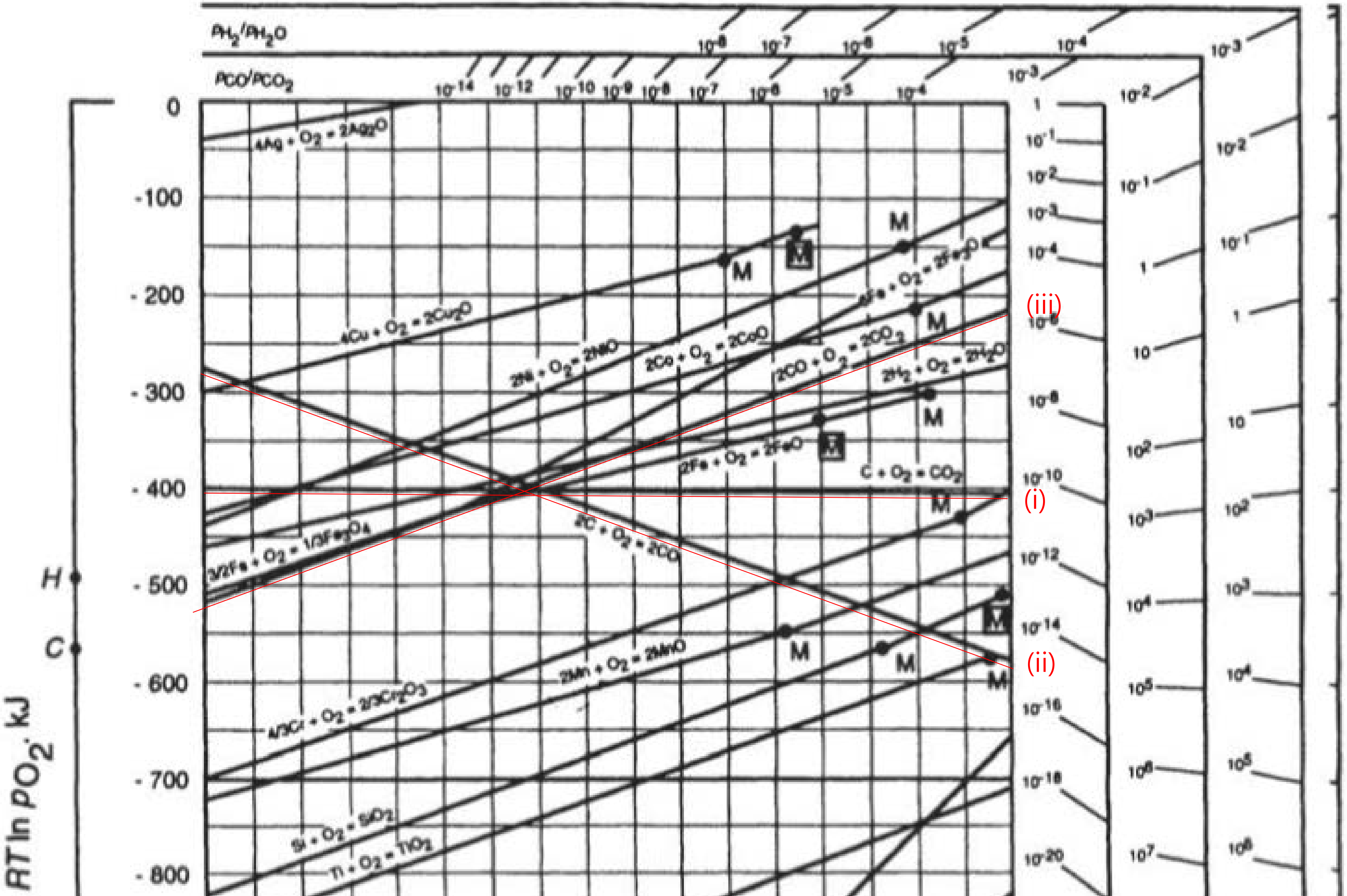
$$2C_{(gr)} + O_{2(g)} = 2CO_{(g)} \quad \text{(ii)} \quad \Delta G^0_{(ii)} = -223{,}400 - 175.3TJ$$

(i) + (ii)

$$2CO_{(g)} + O_{2(g)} = 2CO_{2(g)} \quad \text{(iii)}$$

$$\Delta G^0_{(iii)} = 2\Delta G^0_{(i)} - \Delta G^0_{(ii)} = -564{,}800 + 173.62TJ$$

- (iii) a positive slope (2 moles of gas from 3 moles of gas, $\Delta S^0_{(iii)} = -173.62J/K$)
- (i) virtually no slope (1 moles of gas from 1 moles of gas, $\Delta S^0_{(i)} = 0.84J/K$)
- (ii) negative slope (2 moles of gas from 1 moles of gas, $\Delta S^0_{(ii)} = 175.3J/K$)


P_{H_2}/P_{H_2O}
P_{CO}/P_{CO_2}
10^{-14}
10^{-12}
10^{-10}
10^{-9}
10^{-8}
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1
10
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
10^{7}
10^{8}
10^{-16}
10^{-18}
10^{-20}
0
-100
-200
-300
-400
-500
-600
-700
-800
$RT \ln P_{O_2}$, kJ
H
C
$4Ag + O_2 = 2Ag_2O$
$4Cu + O_2 = 2Cu_2O$
$2Ni + O_2 = 2NiO$
$2Co + O_2 = 2CoO$
$6FeO + O_2 = 2Fe_3O_4$
$2CO + O_2 = 2CO_2$
$2H_2 + O_2 = 2H_2O$
$2Fe + O_2 = 2FeO$
$C + O_2 = CO_2$
$3/2Fe + O_2 = 1/2Fe_3O_4$
$2C + O_2 = 2CO$
$2Mn + O_2 = 2MnO$
$4/3Cr + O_2 = 2/3Cr_2O_3$
$Si + O_2 = SiO_2$
$Ti + O_2 = TiO_2$
M
(i)
(ii)
(iii)

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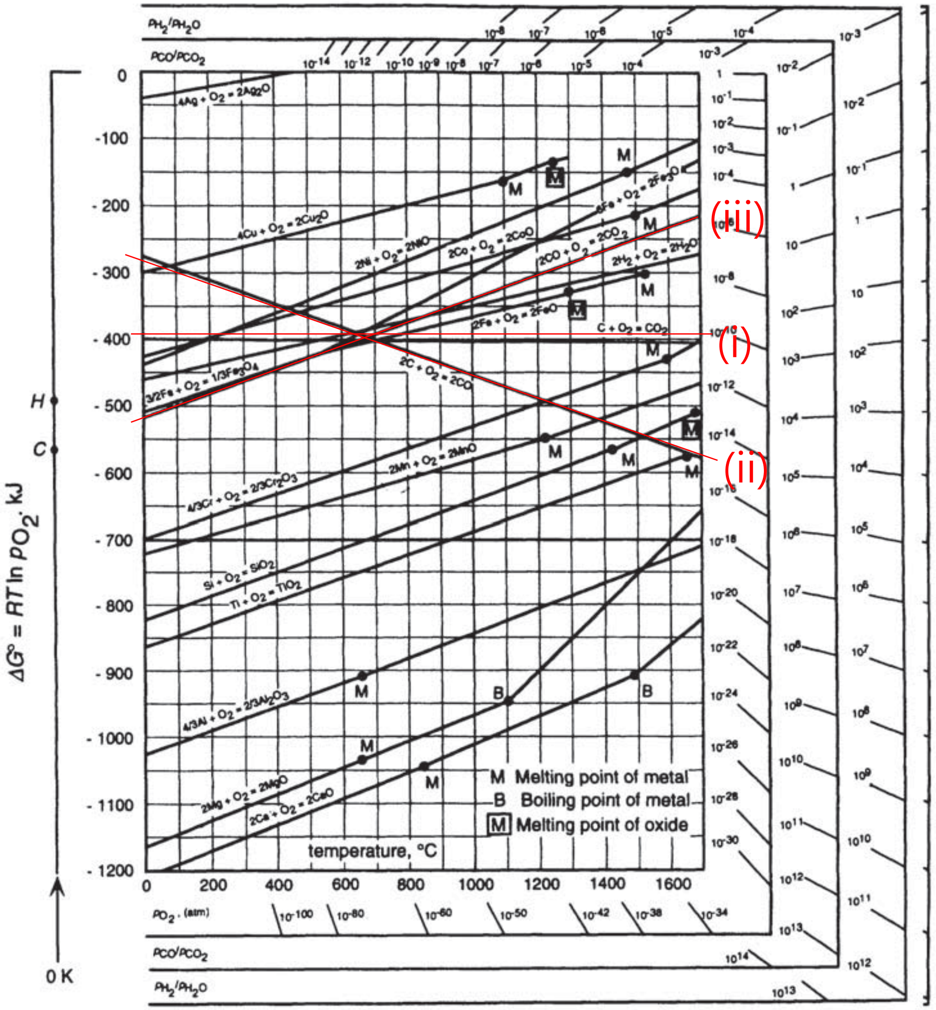

Figure 12.13 The Ellingham diagram for selected oxides.

Consider the equilibrium (ii) - (i)

$$C_{(gr)} + CO_{2(g)} = 2CO_{(g)} \qquad \text{(iv)}$$

$$\Delta G^\circ_{(iv)} = \Delta G^\circ_{(ii)} - \Delta G^\circ_{(i)} = 170,00 - 174.5T$$

$\Delta G^\circ_{(iv)} = 0$ at $T = 978$ K (705 ℃)

⇒ the temperature where (i) and (ii).

Carbon forms two gaseous oxides, CO and CO2, at standard state,

$$p_{CO_2} = p_{CO} = 1$$

Thus, total P = 2 atm. Rxn equilibria under P_{total} = 1 atm, more practical.

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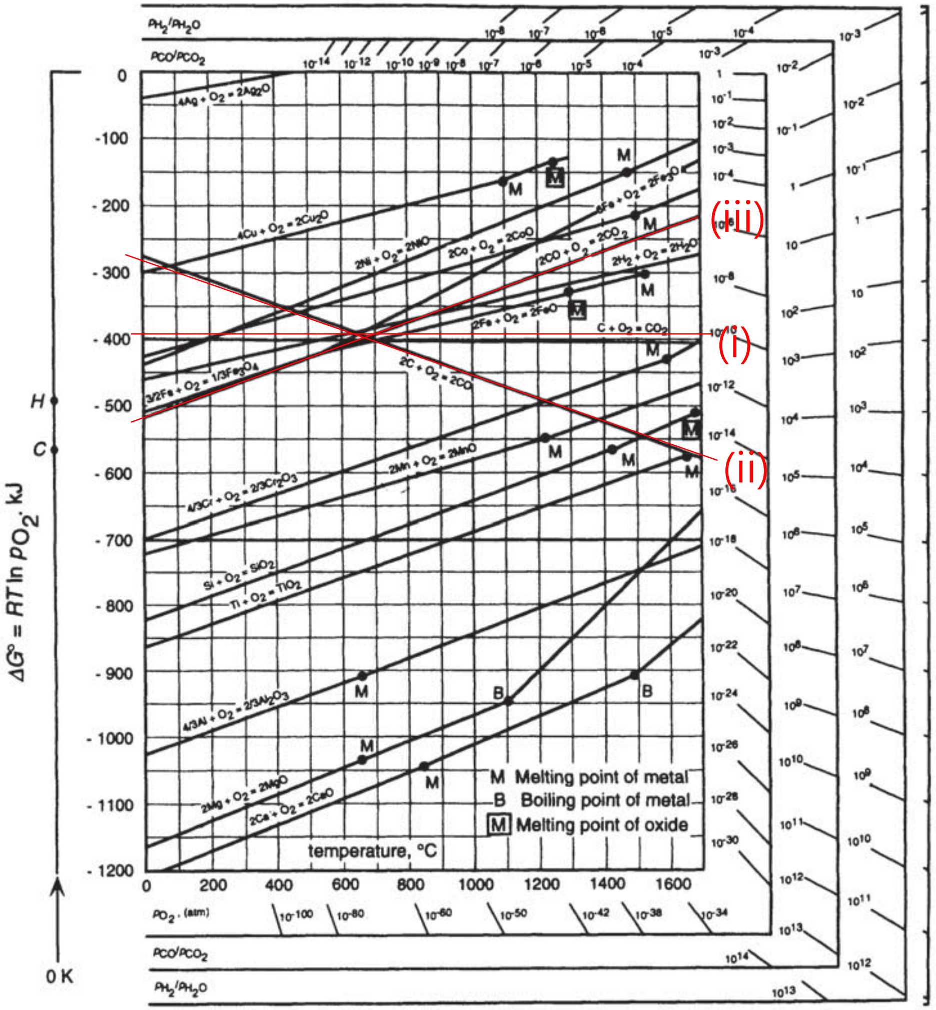

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$$C_{(gr)} + CO_{2(g)} = 2CO_{(g)} \qquad \text{(iv)}$$

$$\Delta G^{\circ}_{(iv)} = \Delta G^{\circ}_{(ii)} - \Delta G^{\circ}_{(i)} = 170{,}00 - 174.5T$$

(i) If P of the system is decreased to 1 atm,

(ii) Thus, if the decrease in P from 2 to 1 atm, and, at the same time maintain $p_{co}=p_{co2}$, T must be decreased.

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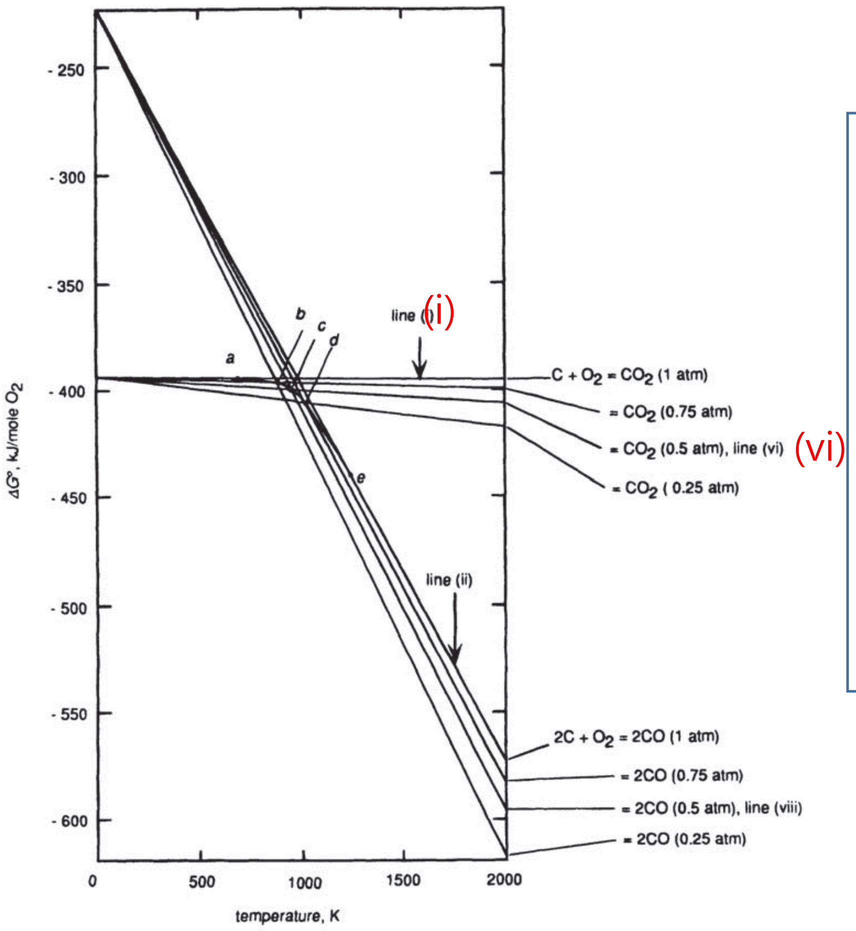

Figure 12.14 The effect of varying the pressures of the product gases of the reactions $C(gr)+O_2(g)$, p=1 atm)=$CO_2(g)$ and $2C(gr)+O_2(g)$,p=1 atm)=$2CO(g)$ on the variations of ΔG with T for the two reactions.

(iii) The T required for $p_{co}=p_{co2}=0.5$ is calculated as follows.
For reaction (i)

This line is obtained by rotating the line for reaction (i) clockwise about its point of intersection with the T=0 axis until, at the temperature T, the vertical separation between line (i) and line (vi) is $RT \ln 0.5$.

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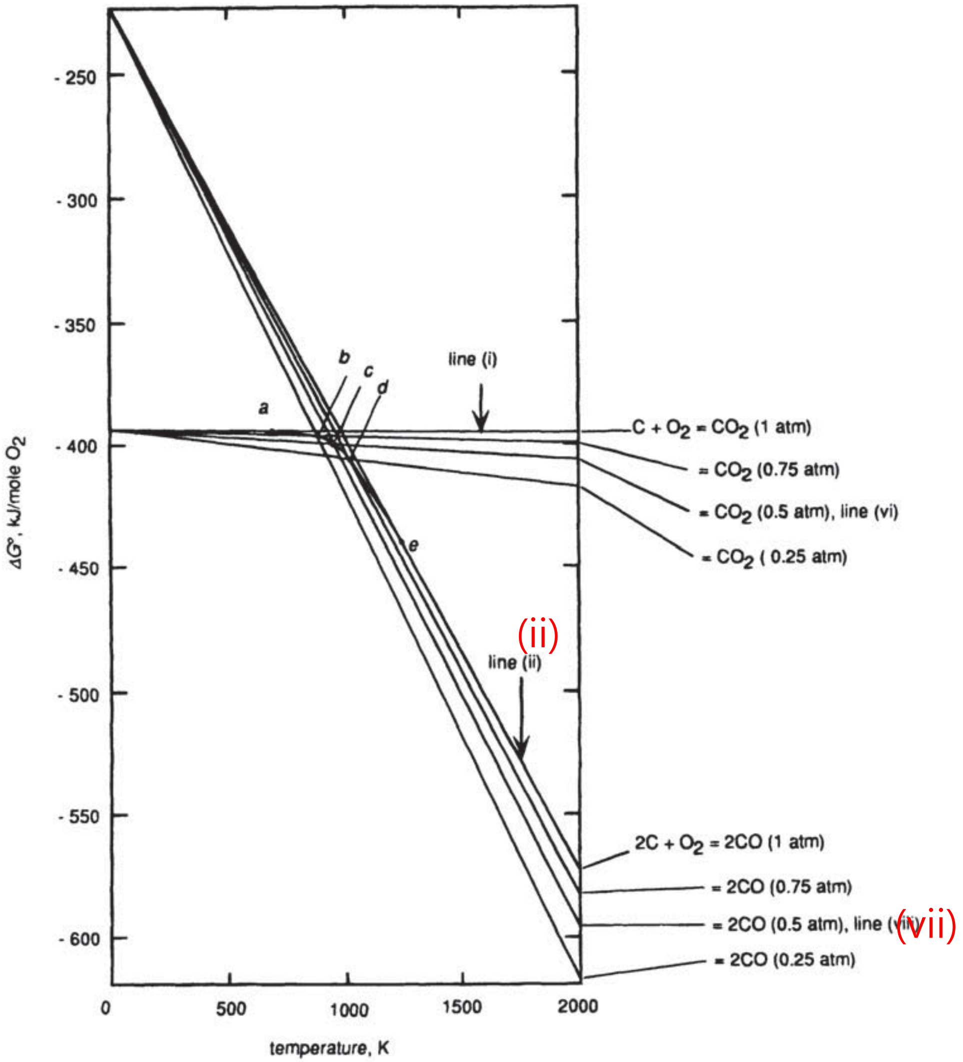

Figure 12.14 The effect of varying the pressures of the product gases of the reactions *C(gr)*+O_2*(g), p*=1 atm)=CO_2(g) and 2C*(gr)*+O_2*(g),p*=1 atm)=2CO*(g)* on the variations of Δ*G* with *T* for the two reactions.

Similarly

$$2C_{(gr)} + O_{2(g)} = 2CO_{(g)} \qquad \text{(ii)} \qquad \Delta G^0_{(ii)} = -223{,}400 - 175.3TJ$$

$$2\mathrm{CO}(T,P = 1\ \mathrm{atm}) \rightarrow 2\mathrm{CO}(T,P = 0.5\ \mathrm{atm}) \qquad \text{(v′)}$$

the Ellingham line for the reaction

$$2\mathrm{C}_{(gr)} + \mathrm{O}_{2(g,P=1\ \mathrm{atm})} = 2\mathrm{CO}_{(g,P=0.5\ \mathrm{atm})} \qquad \text{(vii)}$$

is obtained as the sum of $\Delta G^{\circ}_{(\mathrm{ii})}$ *and* $\Delta G^{\circ}_{(\mathrm{v'})}$ for the change of state

i.e.,

$$\Delta G_{(\mathrm{vii})} = -223{,}400 - 175.3T + 2RT\ln 0.5\ \mathrm{J}$$

This line is obtained by rotating the line for reaction (ii) clockwise about its point of intersection with the *T*=0 axis until, at any *T,* the vertical separation between line (ii) and line (vii) is 2*RT* ln 0.5.

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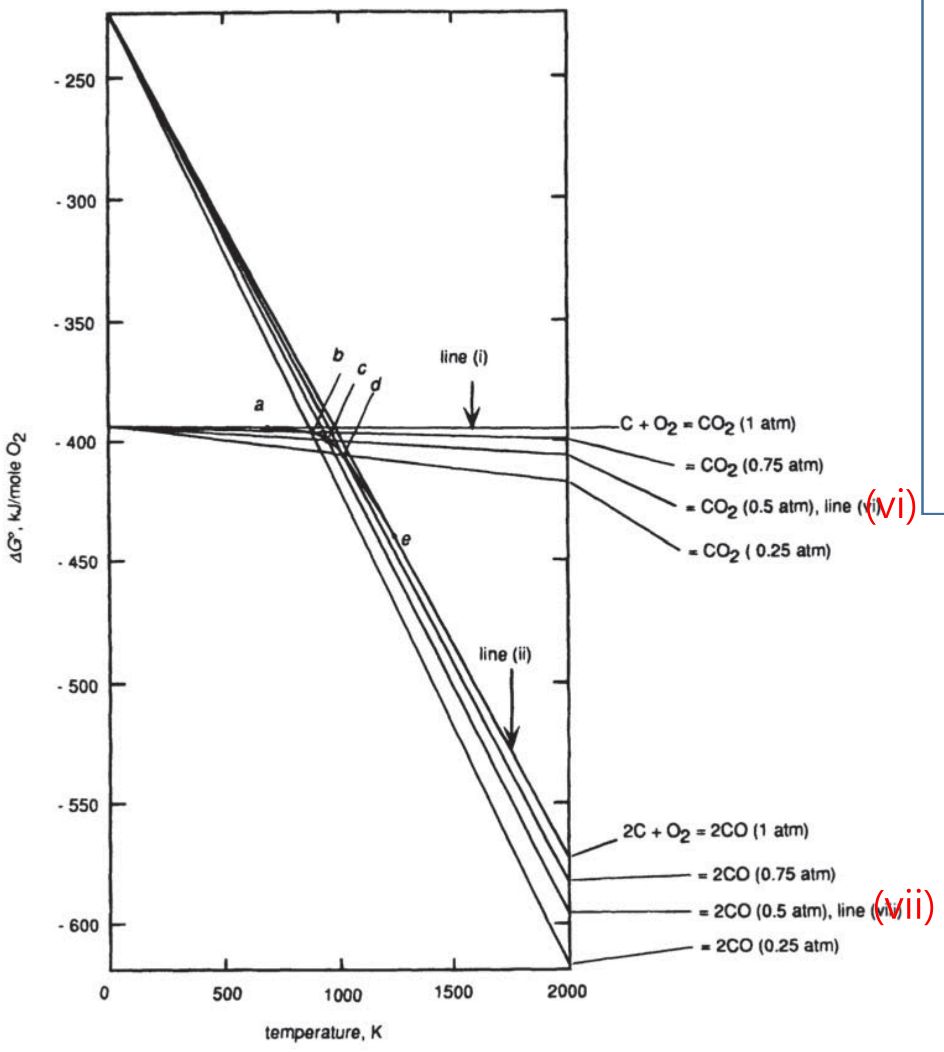
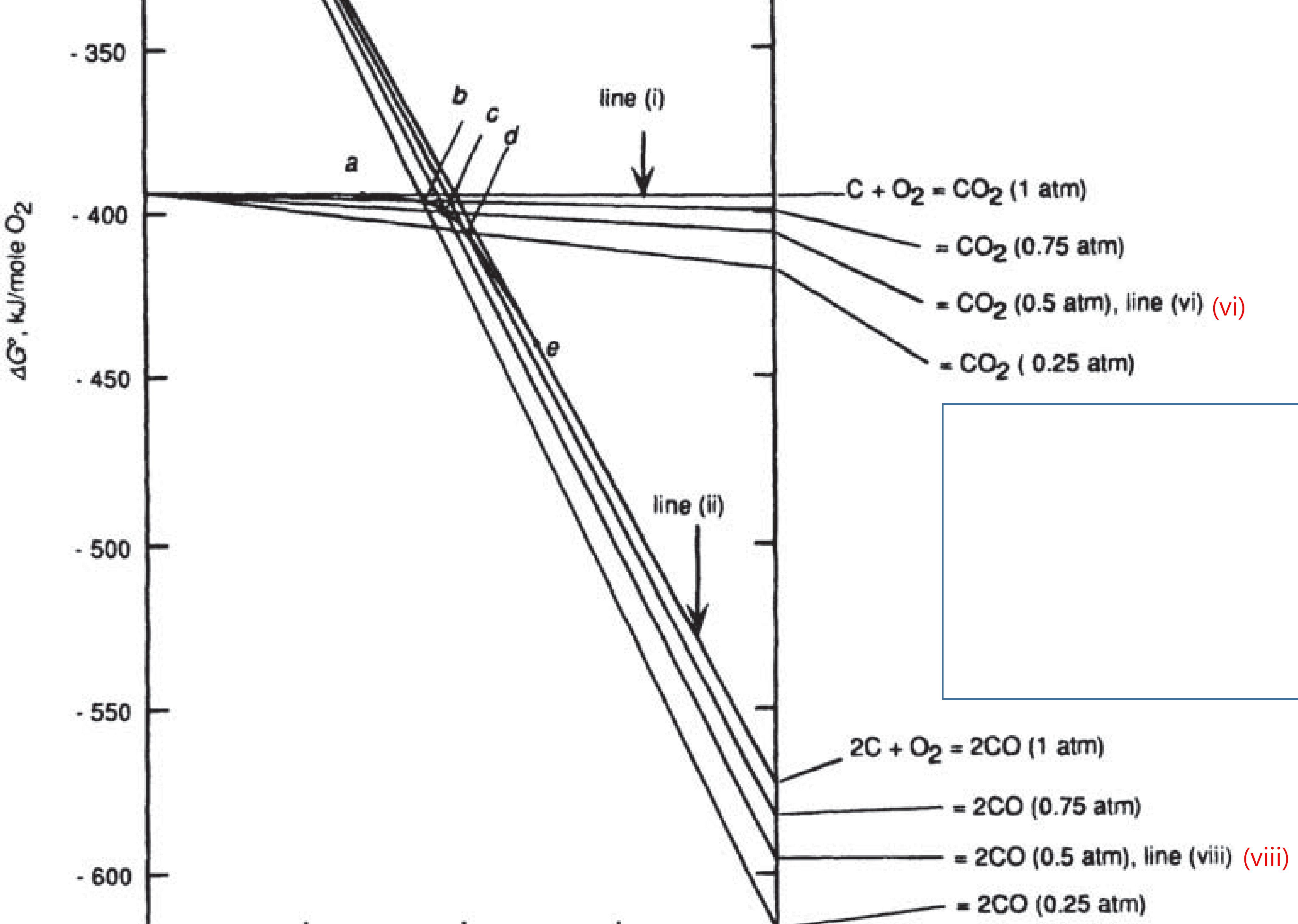


Figure 12.14 The effect of varying the pressures of the product gases of the reactions *C(gr)*+O_2*(g), p*=1 atm)=CO_2(g) and 2C*(gr)*+O_2*(g),p*=1 atm)=2CO*(g)* on the variations of Δ*G* with *T* for the two reactions.

(1) CO_2 and CO, each at 0.5 atm pressure, are in equilibrium with solid C at T of intersection of the lines (vi) and (vii) (the point *c*), where $\Delta G_{(viii)}=0$.

(2) The T at which CO (at 0.25 atm) and CO_2 (at 0.75 atm) are in equilibrium with solid C at the intersection of line (i) rotated clockwise until, at *T*, it has been displaced a vertical distance $RT \ln 0.75$, and line (ii) rotated clockwise until, at *T*, it has been displaced a vertical distance $2RT \ln 0.25$. (the point *b*).

(3) the point *d* at which CO at 0.75 atm pressure and CO_2 at 0.25 atm pressure are in equilibrium with solid C.


- 350
- 400
- 450
- 500
- 550
- 600
ΔG°, kJ/mole O2
a
b
c
d
e
line (i)
line (ii)
C + O2 = CO2 (1 atm)
= CO2 (0.75 atm)
= CO2 (0.5 atm), line (vi)
(vi)
= CO2 (0.25 atm)
2C + O2 = 2CO (1 atm)
= 2CO (0.75 atm)
= 2CO (0.5 atm), line (viii)
(viii)
= 2CO (0.25 atm)

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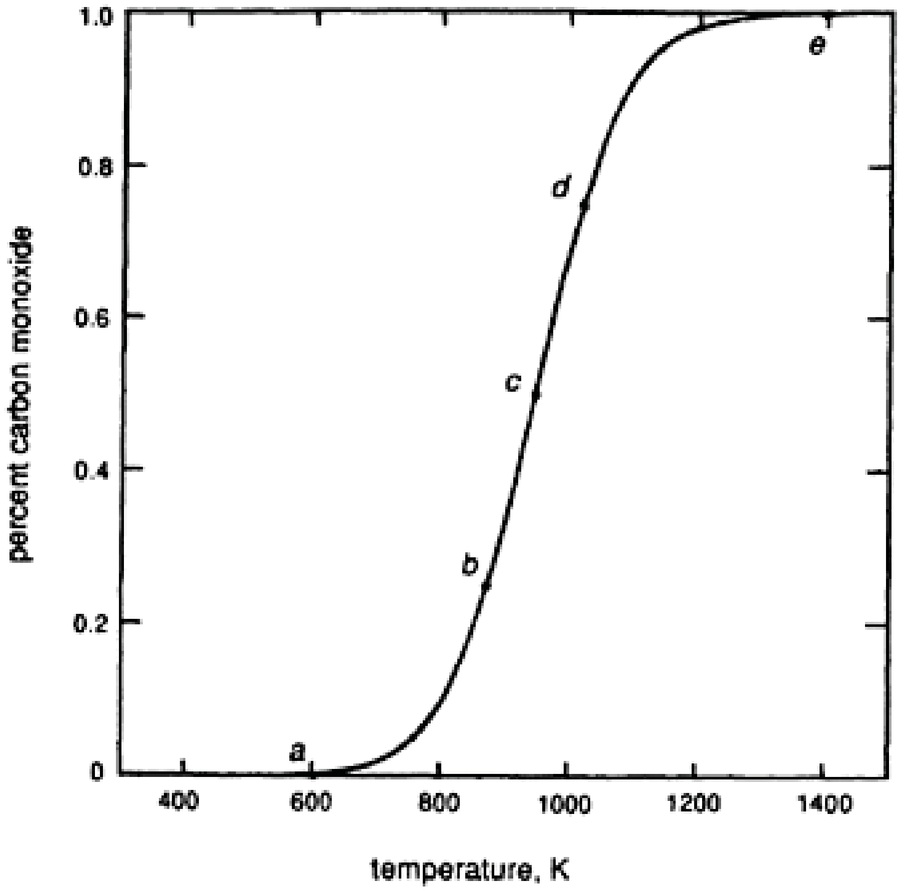

Figure 12.15 The variation, with temperature, of the composition of the CO–CO_2 gas mixture in equilibrium with solid C at P_{total}=1 atm.

Line a-b-c-d-e is the locus of P_{total} = 1 atm with varying CO, CO2, pressure.

1. At T < 600 K, the equilibrium gas is virtually CO_2 at P=1 atm. (a)
2. T>1400 K, the equilibrium gas is virtually CO at at P=1 atm.(e)

At any *T*, the CO–CO_2 mixture in equilibrium with C exerts an equilibrium oxygen pressure, $P_{O_{2(eq.T)}}$, via the equilibrium

$$2CO + O_2 = 2CO_2 \qquad \text{(iii)}$$

$$\Delta G^\circ_{(iii)} = -564{,}800 + 173.62T \text{ J} = -RT\ln\left(\frac{p^2_{CO_2}}{p^2_{CO}\,p_{O_2}}\right)$$

$$= 2RT\ln\left(\frac{p_{CO}}{p_{CO_2}}\right)_{\text{eq. with C}} + RT\ln p_{O_2(\text{eq.})}$$

$$\ln p_{O_2(\text{eq.}T)} = -\frac{564{,}800}{8.3144T} + \frac{173.62}{8.3144} + 2\ln\left(\frac{p_{CO_2}}{p_{CO}}\right)_{\text{eq. with C}} \qquad (12.12)$$

For M+O_2=MO_2, if solid C is to reduce MO_2 at *T*, then $P_{O_2(T)} < P_{O_2(eq.T)}$

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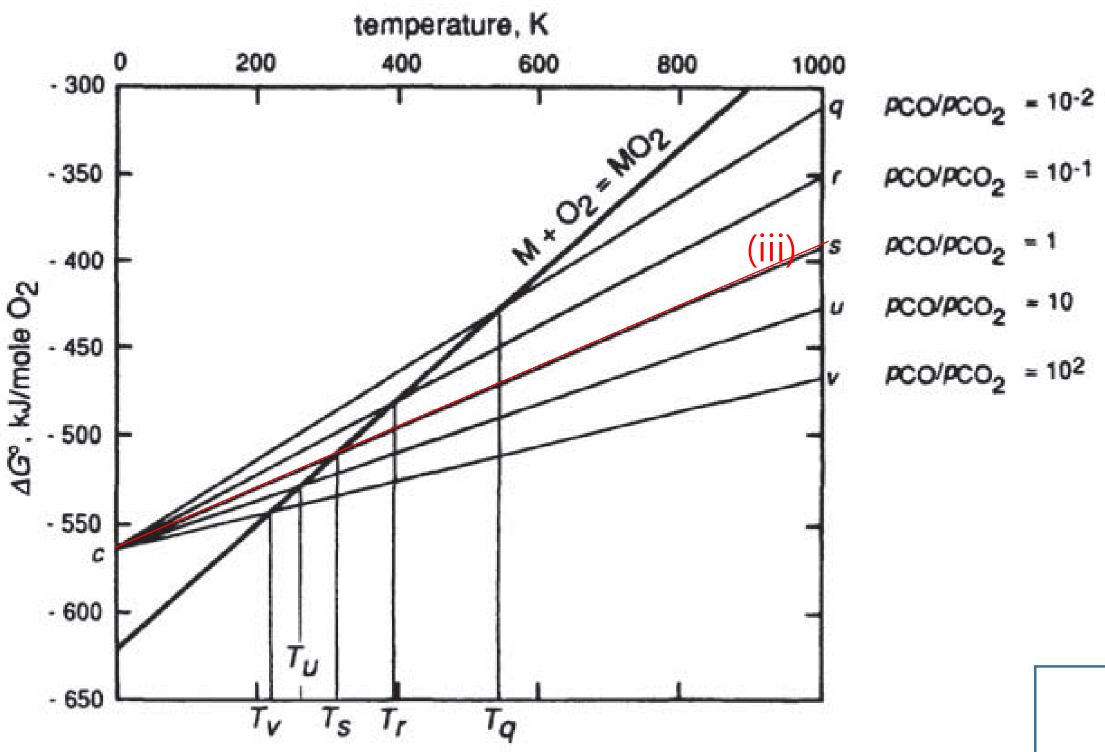

Figure 12.16 Illustration of the effect of the ratio ${}^{P_{CO_2}}/_{P_{CO}}$ in a $CO_2 - CO$ gas mixture on the temperature at which the equilibrium $M+CO_2=MO+CO$ is established.

The Equilibrium $2CO+O_2=2CO_2$

(i) The Ellingham line for the reaction = the line *cs.*

The variation of $\Delta G°$ with T, this line is for the reaction which produces CO_2 at 1 atm from CO at 1 atm and O_2 at 1 atm.

The effect of producing the CO_2 at any pressure, *P,* other the 1 atm (from CO and O_2 each at 1 atm) is the rotation of the line *cs* about the point *c,* clockwise if *P*<1 atm and anticlockwise if *P*>1 atm.

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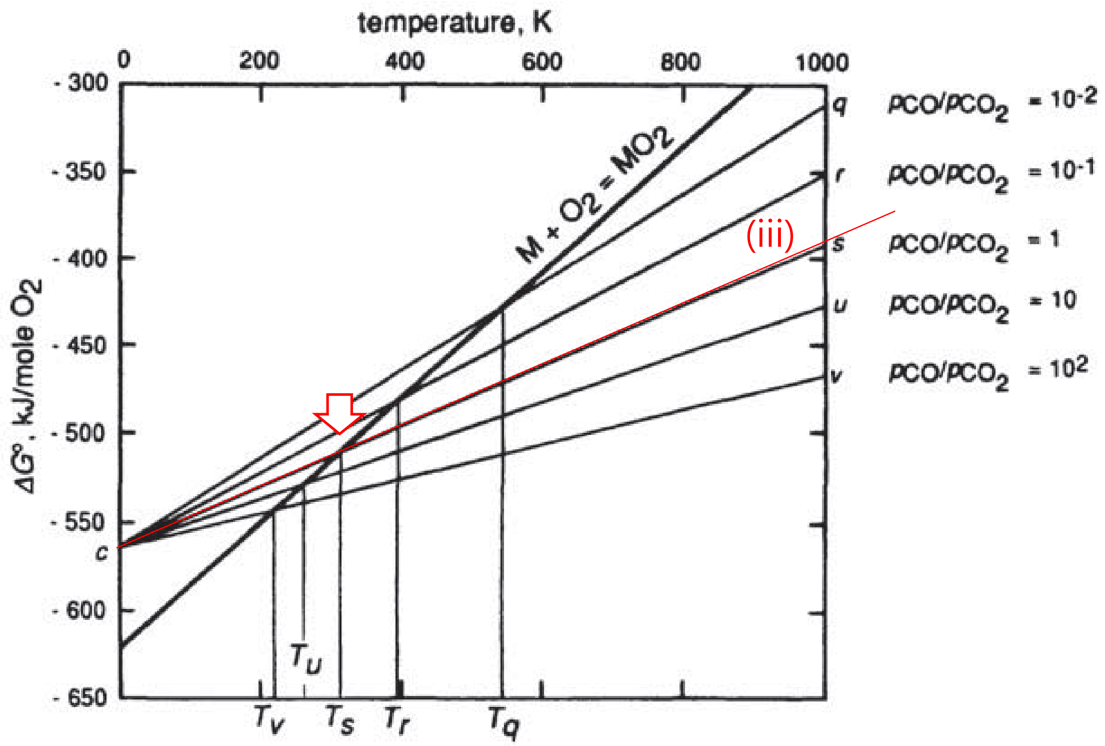


Figure 12.16 Illustration of the effect of the ratio $^{p_{CO_2}}/_{p_{CO}}$ in a $CO_2 - CO$ gas mixture on the temperature at which the equilibrium $M+CO_2=MO+CO$ is established.

(ii) The Ellingham line for the reaction $M+O_2=MO_2$

This intersects the line *cs* at *Ts*, which is thus the temperature at which $\Delta G^0_{(iii)}$ for the reaction

$$MO_2 + 2CO = M + 2CO_2 \qquad \text{(ix)}$$

is zero, i.e.,

$$\Delta G^\circ_{(ix)} \text{ at } T_s = 0 = -RT \ln \left(\frac{p_{CO_2}}{p_{CO}} \right)^2$$

and thus

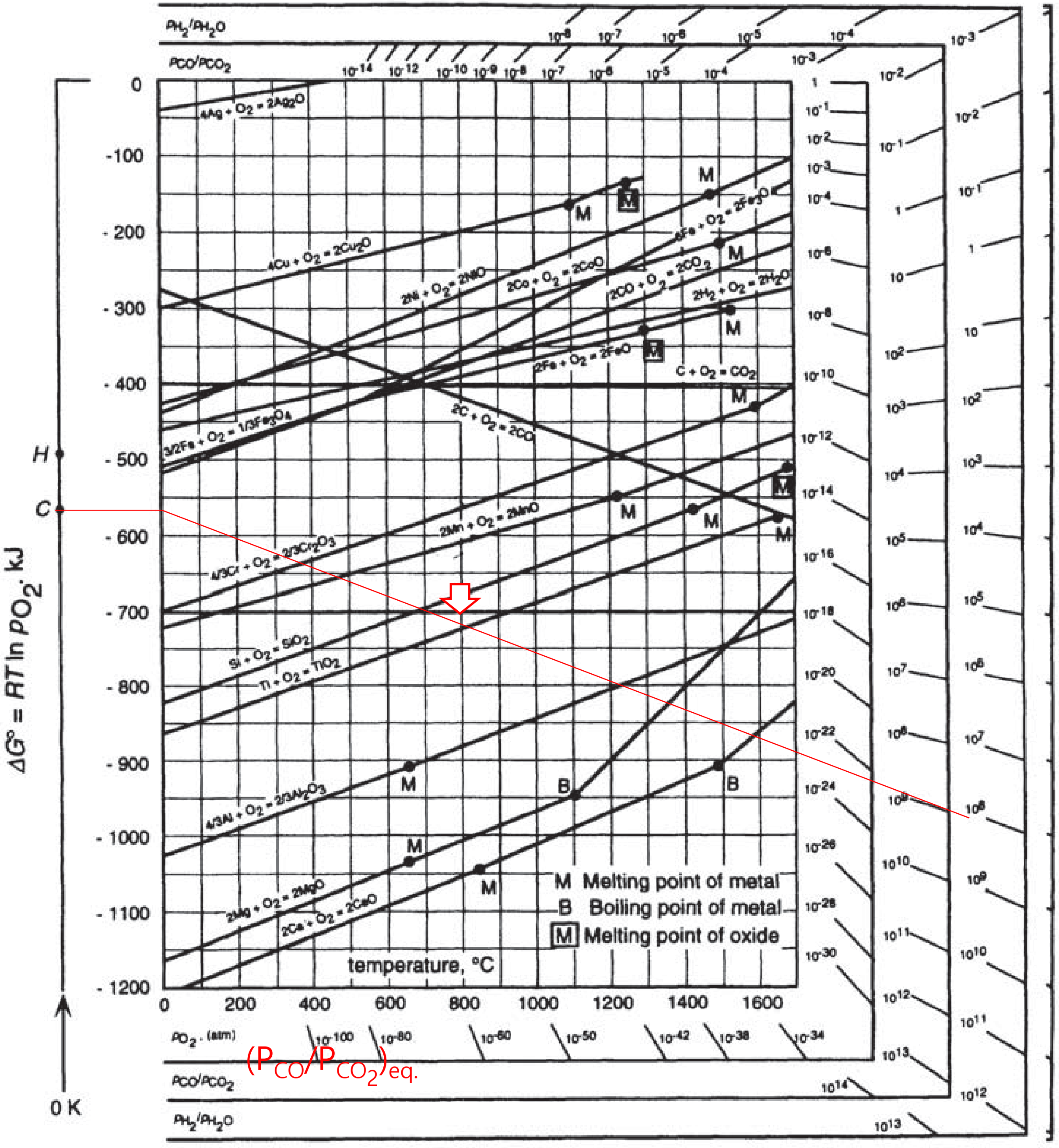
$$\frac{p_{CO_2}}{p_{CO}} = 1$$

The Ellingham line for the reaction $M+O_2=MO_2$ intersects the line *cu* at T_u, and T_u is thus the temperature at which the reaction

$$MO_2 + 2CO(1\text{ atm}) = M + 2CO_2(0.1\text{ atm}) \quad \text{(x)}$$

is at equilibrium, i.e.,

$$\Delta G_{(x)} \text{ at } T_u = \Delta G^\circ_{(ix)} + 2RT \ln 0.1$$



But, by definition,

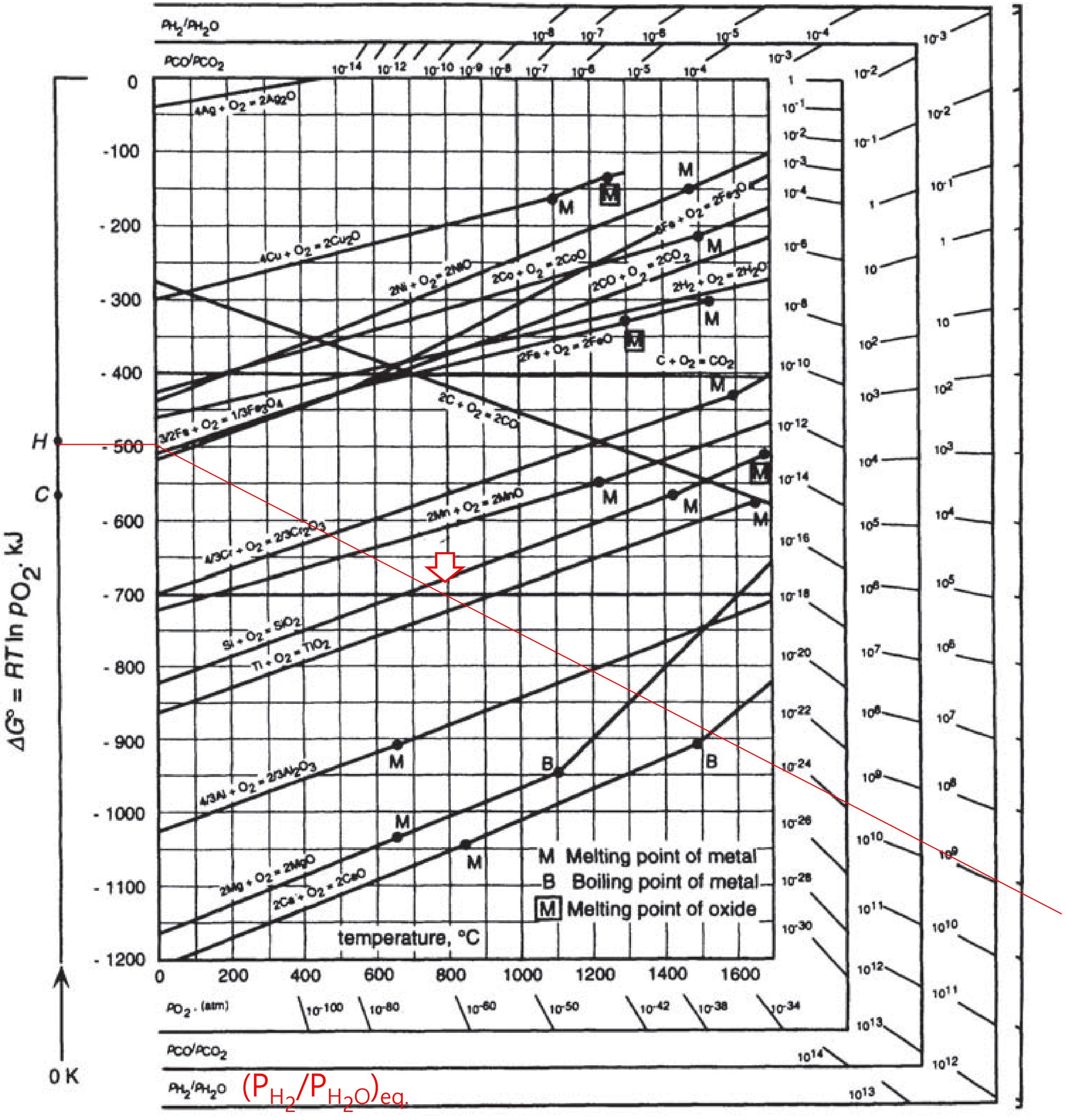
$$\Delta G^\circ_{(\mathrm{ix})} = -RT \ln \left(\frac{p_{CO_2}}{p_{CO}} \right)^2_{\mathrm{eq}}$$

and thus

$$\Delta G_{(\mathrm{x})} = 0 = -2RT \ln \left(\frac{p_{CO_2}}{p_{CO}} \right)_{\mathrm{eq}} + 2RT \ln 0.1$$

At T_u calculation gives $(P_{CO}/P_{CO_2})_{eq.} = 10$.
If T is decreased to T_u from T_s, the ratio must increase from 1 to 10 to maintain the rxn equilibrium.

At T_q calculation gives $(P_{CO}/P_{CO_2})_{eq.} = 0.01$.
If T is increased to T_q from T_s, the ratio must decrease from 1 to 0.01 to maintain the rxn equilibrium.



Similarly, the H_2/H_2O nomographic scale is added by considering the effect of the variation of the pressure of H_2O on the reaction equilibrium

$$2H_2 + O_2 = 2H_2O$$

The equilibrium H_2/H_2O ratio at *T* for the reaction

$$MO_2 + 2H_2 = M + 2H_2O$$

is read off the H_2/H_2O scale as the point which is collinear with the points *H* and for the reaction $M+O_2=MO_2$.

12. 7 Graphical Representation of Equilibria in The System Metal-Carbon-Oxygen

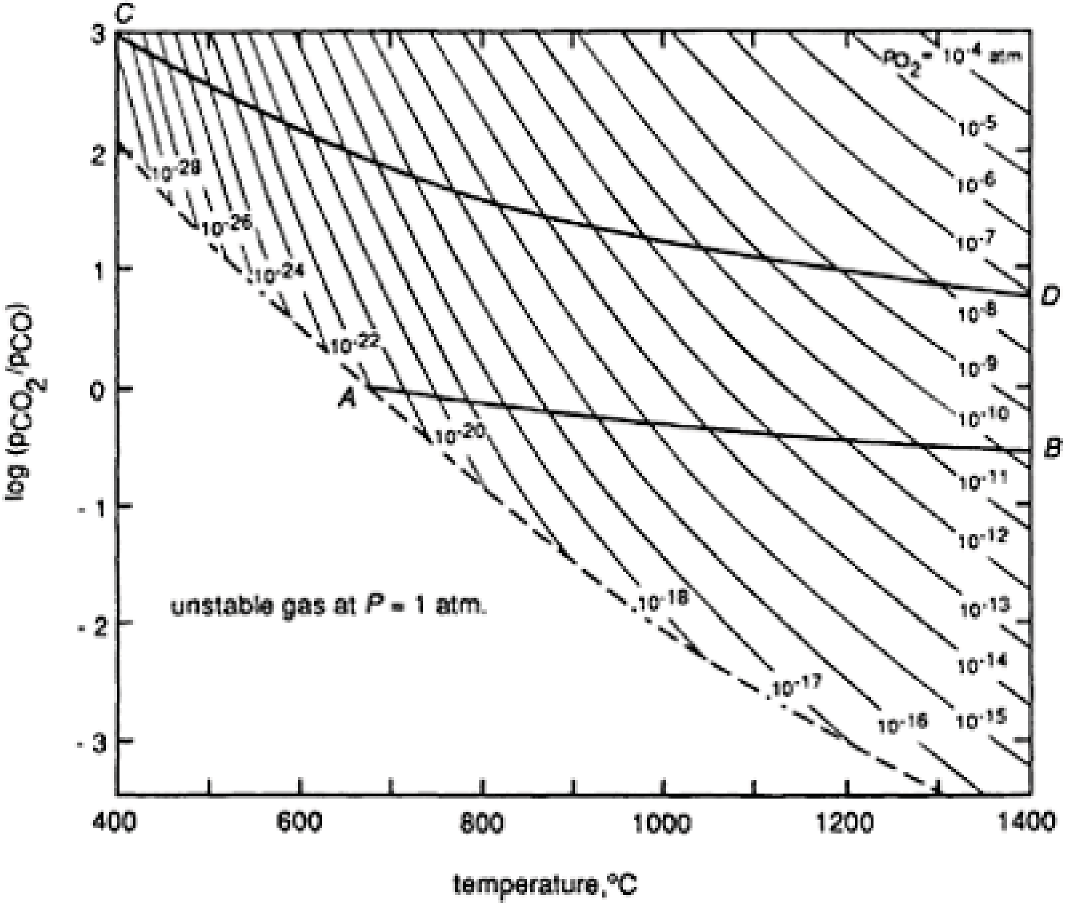


Figure 12.17 The relationship between the partial pressure of oxygen in a CO_2– CO gas mixture and temperature. The broken line is the variation, with temperature, of the composition of the gas which is in equilibrium with graphite at 1 atm pressure. The lines *AB* and *CD* represent, respectively, the equilibria Fe+CO_2=FeO+CO and Co+CO_2=CoO+CO.

As the nomographic scale for the ratio CO/CO_2 in Fig. 12.13 shows that the range of interest of values of ${}^{P_{CO}}/_{P_{CO_2}}$ is 10^{-14} to 10^{14}, it is convenient to present this ratio on a logarithmic scale. Fig. 12.17, which uses the coordinates log $({}^{P_{CO}}/_{P_{CO_2}})$ and *T,* represents a convenient method of clear presentation of reaction equilibrium in the carbon–oxygen and carbon–oxygen–metal systems.
From Eq. (iii), for

$$2CO_{(g)} + O_{2(g)} = 2CO_{2(g)}$$

$$\Delta G^{\circ}_{\text{(iii)}} = -546{,}800 + 173.62T \text{ J}$$

$$= -RT \ln\left(\frac{p^2_{CO_2}}{p^2_{CO}p_{O_2}}\right)$$

and thus

$$\log\left(\frac{p_{CO_2}}{p_{CO}}\right) = \frac{1}{2}\log p_{O_2} + \frac{564{,}800}{2 \times 2.303 \times 8.3144T} - \frac{173.62}{2 \times 2.303 \times 8.3144}$$

12. 7 Graphical Representation of Equilibria in The System Metal-Carbon-Oxygen

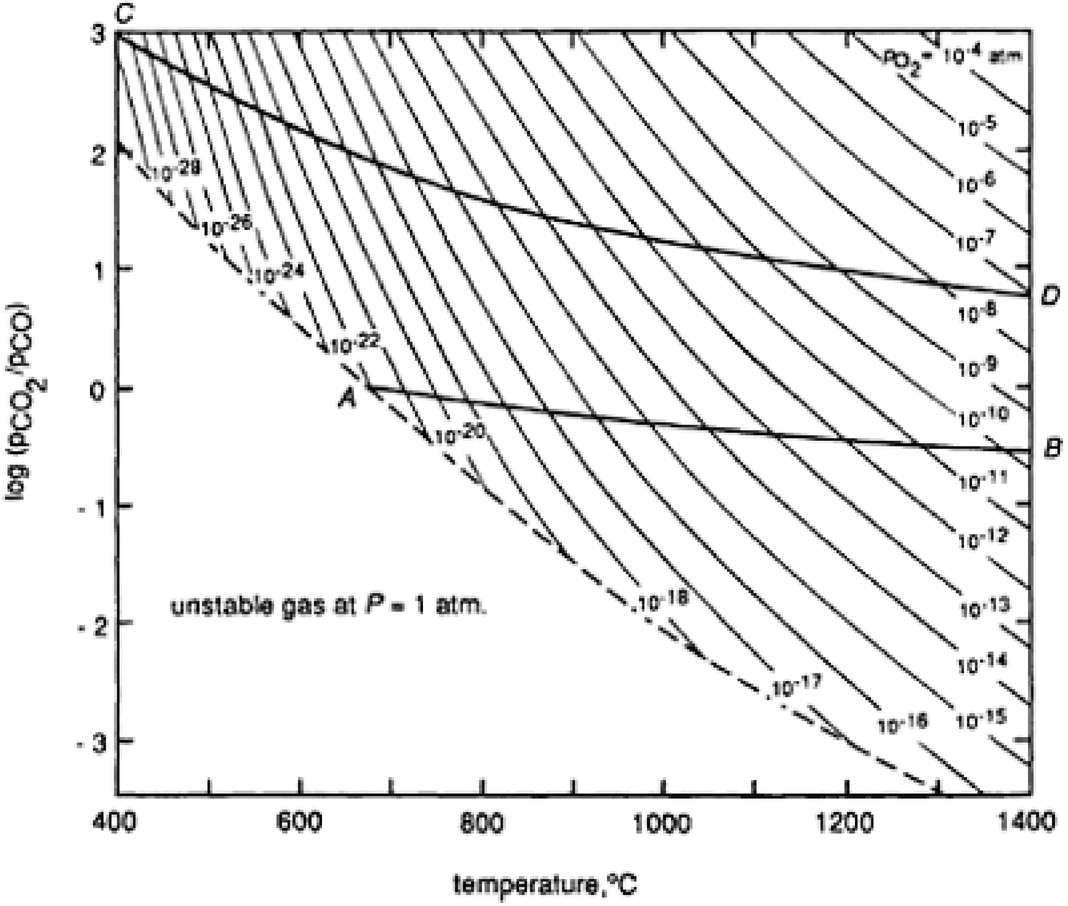


Figure 12.17 The relationship between the partial pressure of oxygen in a CO_2– CO gas mixture and temperature. The broken line is the variation, with temperature, of the composition of the gas which is in equilibrium with graphite at 1 atm pressure. The lines *AB* and *CD* represent, respectively, the equilibria $Fe+CO_2=FeO+CO$ and $Co+CO_2=CoO+CO$.

The equilibrium

$$C_{(gr)} + CO_{2(g)} = 2CO_{(g)}$$

sets a lower limit on the CO2/CO ratio which can be obtained at any temperature,

$$\Delta G^\circ_{(iv)} = 170{,}700 - 174.5T\ \text{J} = -RT\ln\left(\frac{p^2_{CO}}{p_{CO_2}}\right)$$

and thus, at a total pressure of 1 atm, i.e., when $P_{CO_2} = 1 - P_{CO}$

$$\frac{p^2_{CO}}{1-p_{CO}} = \exp\left(\frac{-170{,}700}{8.3144T}\right)\exp\left(\frac{174.5}{8.3144}\right) = x$$

or

$$p^2_{CO} + p_{CO}x - x = 0$$

$$p_{CO} = \frac{-x + \sqrt{x^2+4x}}{2}$$

$$p_{CO_2} = \frac{2 + x - \sqrt{x^2+4x}}{2}$$

$$\frac{p_{CO_2}}{p_{CO}} = \frac{2 + x - \sqrt{x^2+4x}}{\sqrt{x^2+4x} - x}$$

12. 7 Graphical Representation of Equilibria in The System Metal-Carbon-Oxygen

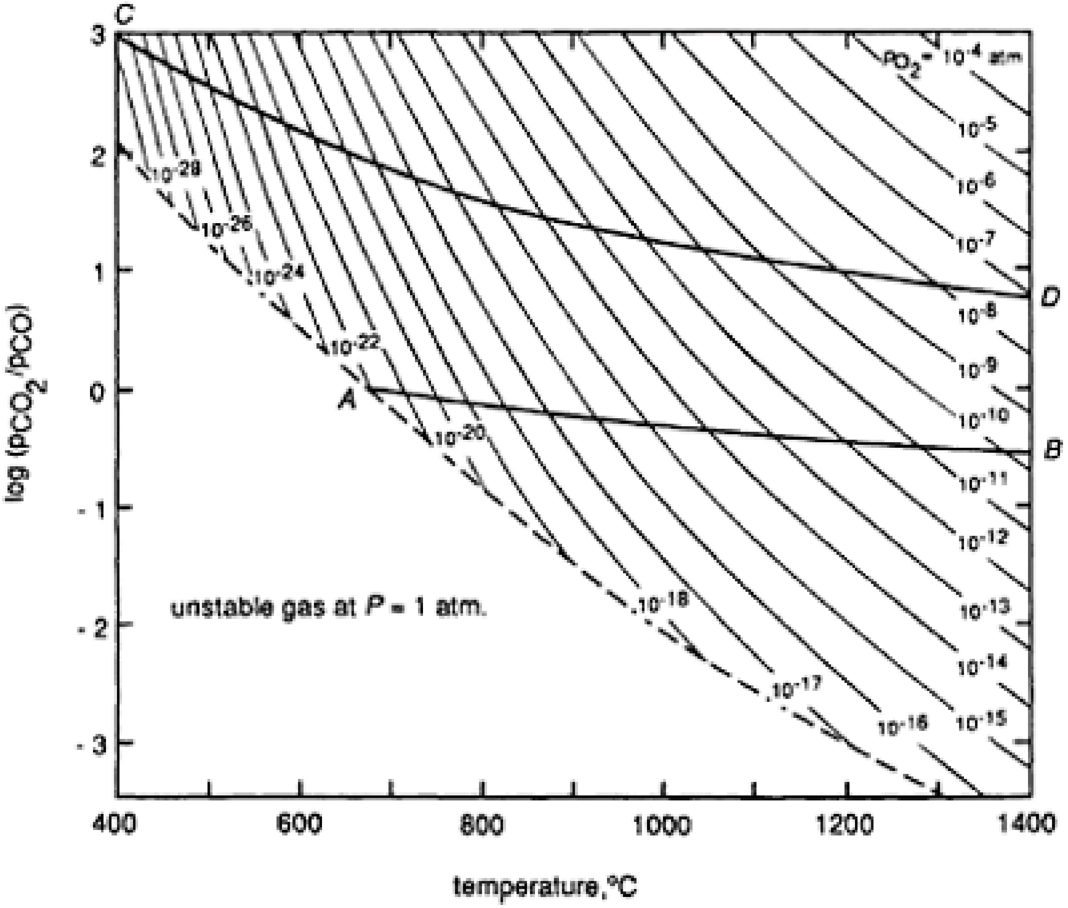


Figure 12.17 The relationship between the partial pressure of oxygen in a CO_2– CO gas mixture and temperature. The broken line is the variation, with temperature, of the composition of the gas which is in equilibrium with graphite at 1 atm pressure. The lines *AB* and *CD* represent, respectively, the equilibria Fe+CO_2=FeO+CO and Co+CO_2=CoO+CO.

Equilibria such as

$$FeO_{(s)} + CO_{(g)} = Fe_{(s)} + CO_{2(g)}$$

$\Delta G°$=-22,800+24.26T J and thus the variation of the equilibrium ratio CO_2/CO with temperature is given by

$$\log\left(\frac{p_{CO_2}}{p_{CO}}\right)_{eq.FeO/Fe} = \frac{22{,}800}{2.303 \times 8.3144T} - \frac{24.26}{2.303 \times 8.3144}$$

i.e., it is the temperature at which

$$p_{O_2(eq.C/CO/CO_2)} = p_{O_2(eq.Fe/FeO)}$$

The line *CD* in Fig. 12.17 represents the variation of log (P_{CO_2}/P_{CO}) with *T* for the equilibrium

$$CoO_{(s)} + CO_{(g)} = Co_{(s)} + CO_{2(g)}$$

for which

$$\Delta G° = -48{,}500 + 14.9T \text{ J}$$

and

$$\log\left(\frac{p_{CO_2}}{p_{CO}}\right)_{eq.Co/CoO} = \frac{48{,}500}{2.303 \times 8.3144T} - \frac{14.9}{2.303 \times 8.3144}$$

12. 7 Graphical Representation of Equilibria in The System Metal-Carbon-Oxygen

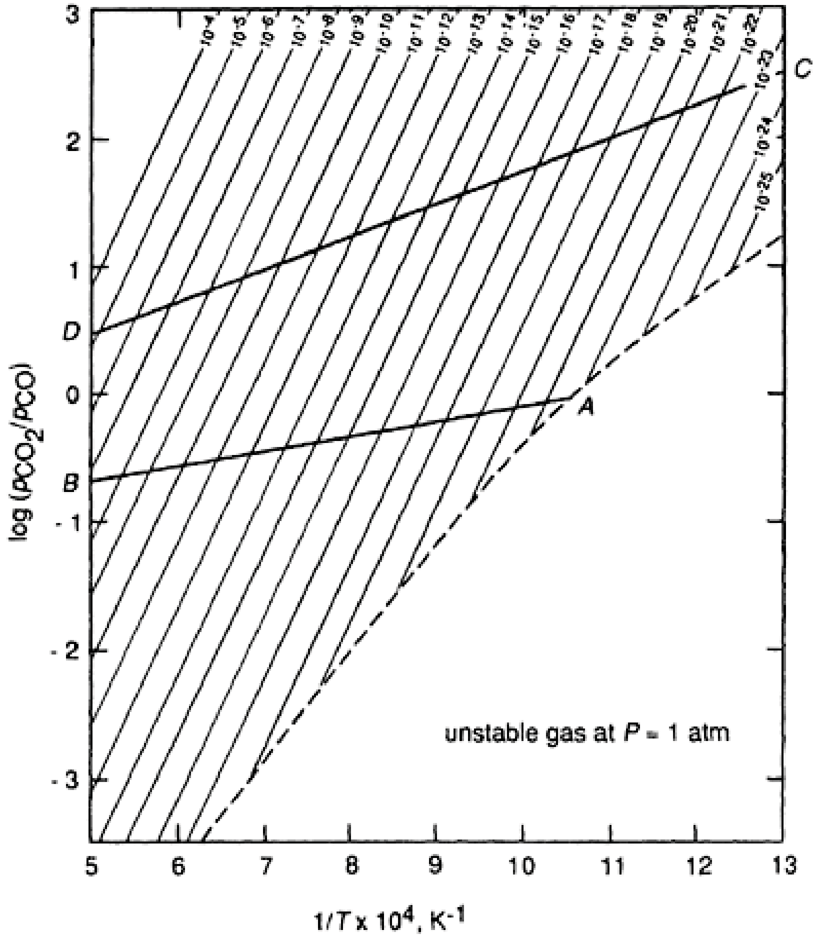


Figure 12.18 Fig. 12.17 reproduced as log ($^{P_{CO_2}}/_{P_{CO}}$) vs. 1/T.

With respect to the amount of information which can be obtained from a graphical representation of equilibria in a system, Fig. 12.18 is a better representation than is Fig. 12.17. As

$$\left[\frac{\partial \ln K}{\partial\left(\frac{1}{T}\right)}\right] = -\frac{\Delta H^\circ}{R}$$

the slope of a tangent to an equilibrium line at the temperature T gives the value of $^{-\Delta H^0}/_{R}$. If $\Delta C_p = 0$, log K is a linear function of $1/T$.