THERMODYNAMICS

ΔU represents the change of internal energy

ΔE represents the change of total energy from an initial state to a final state.

First Law of Thermodynamics

$$\Delta U + \Delta E_k + \Delta E_p = \pm Q \pm W$$

+ve from surroundings to system
-ve from system to surroundings
(for heat: +ve endothermic
-ve exothermic

$$\Delta U = Q$$

$$dU = dQ$$

enthalpy, H

$$dH = dU + d(PV)$$

$$dH = dQ$$

$$\Delta H = Q$$

Entropy

Second Law of Thermodynamics

the entropy change of all processes must be positive.

$$dS = \frac{dQ_{rev}}{T}$$

$$\Delta S = \frac{Q}{T}$$

$$\Delta S = \frac{\Delta H}{T}$$

Entropy also plays a role in the Third Law of Thermodynamics, which states that *the entropy of a perfect crystal is zero at zero absolute temperature.*

Gibbs free energy, G

$$G = H - TS$$

$$dG = dH - TdS$$

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

Table 2.1 Summary of Free Energy Effects on Process Spontaneity

$\Delta G < 0$	Process proceeds spontaneously
$\Delta G > 0$	Process not spontaneous
$\Delta G = 0$	Process at equilibrium

Chemical Potential

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{P,S,n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$$

Gibbs Phase Rule.

Component

A component is a chemical constituent (element or compound) that has a specified composition.

Phase

A phase is defined as a homogeneous portion of a system that has uniform physical and chemical characteristics. It need not be continuous.

Degree of Freedom

The degrees of freedom are the number of variables (including composition) that must be specified in order for the system to be defined in a strict, mathematical sense.


140
CALORIES
PER CAN
12 FL OZ
(355 mL)

Gibbs Phase Rule.

One component system (A)
Two phases (α and β) in equilibrium

Means:

$$T_\alpha = T_\beta$$

$$P_\alpha = P_\beta$$

$$\mu_\alpha = \mu_\beta$$

But:

$$\mu_\alpha = \mu_\alpha(T_\alpha, P_\alpha)$$

$$\mu_\beta = \mu_\beta(T_\beta, P_\beta)$$

So, three equations and four unknown intensive variables

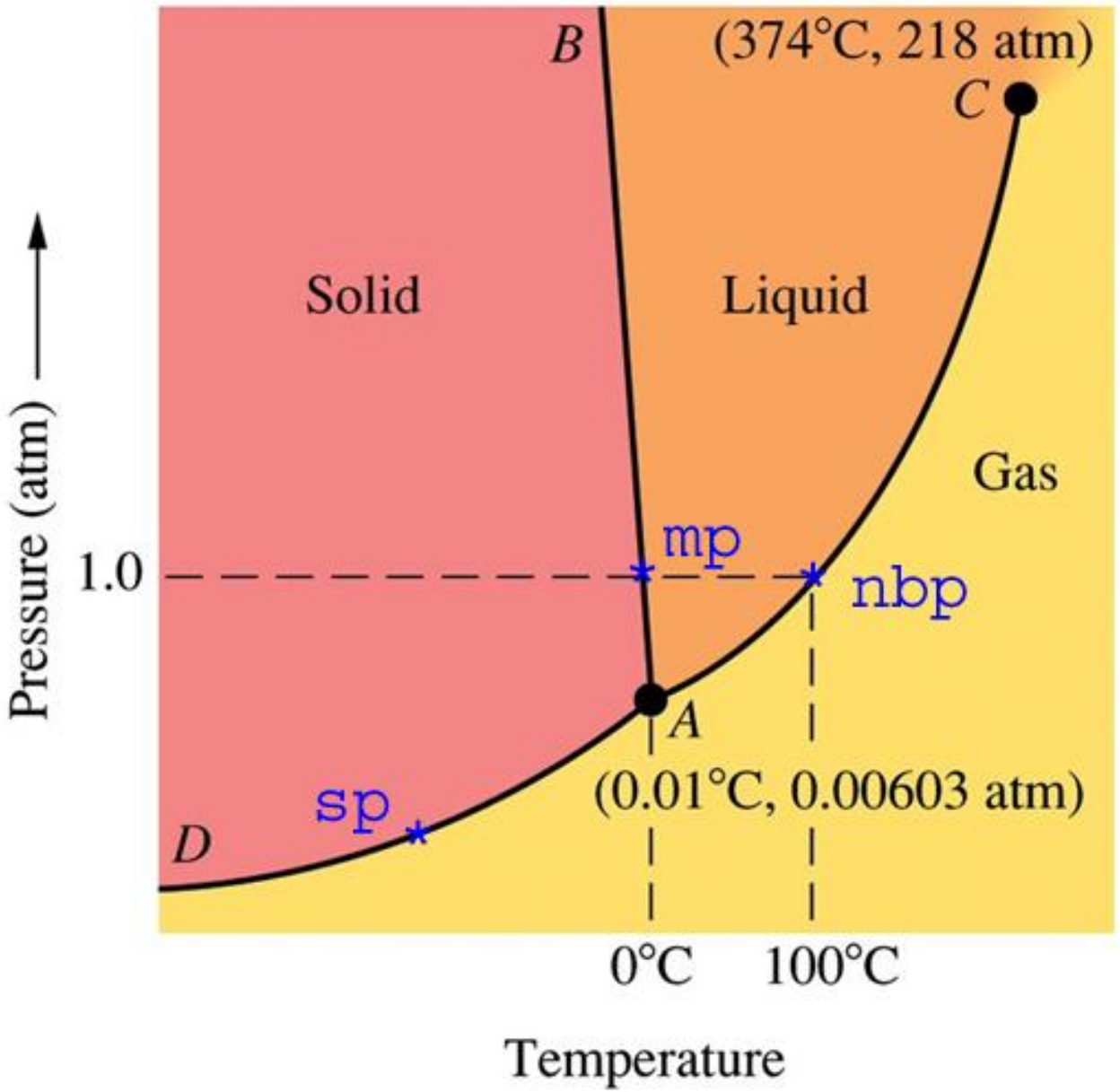
$$T_\alpha,\ P_\alpha,\ T_\beta, \text{ and } P_\beta$$

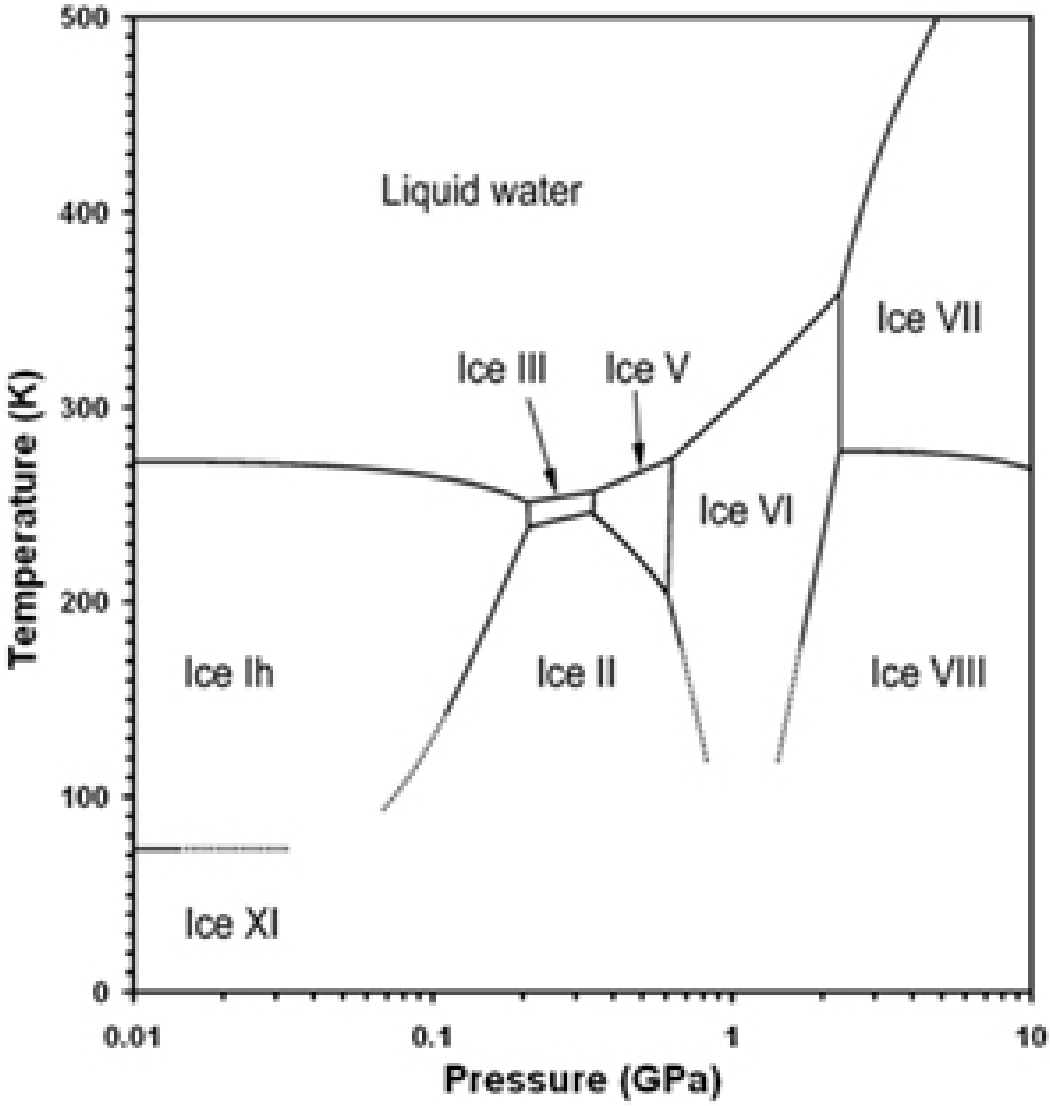
Gibbs Phase Rule.

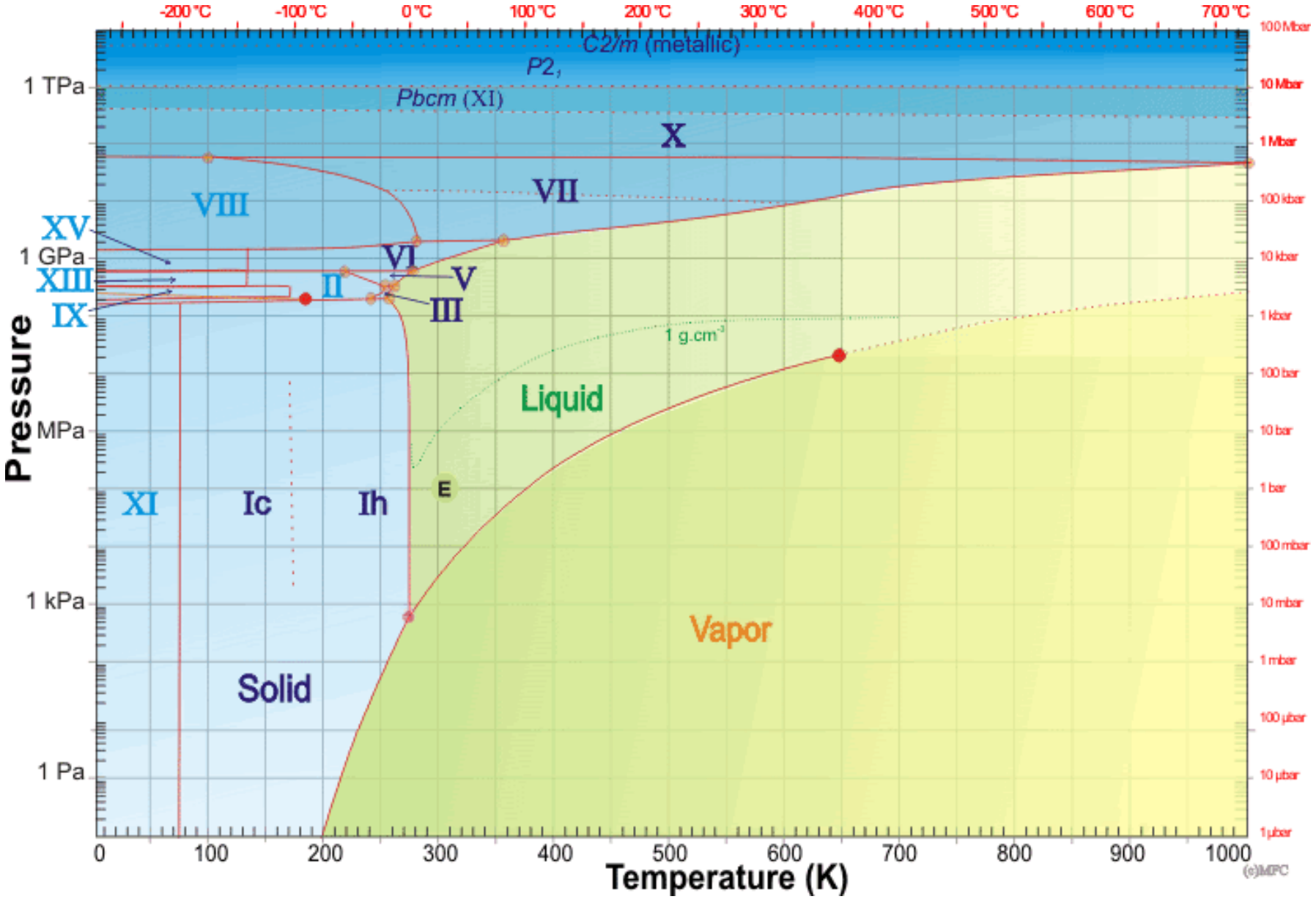
Generalizing to a system with C components and ϕ phases

$$F = C - \phi + 2$$

$$F = C - \phi + N$$


B
(374°C, 218 atm)
C
Solid
Liquid
Gas
Pressure (atm)
1.0
mp
nbp
A
(0.01°C, 0.00603 atm)
sp
D
0°C
100°C
Temperature


Liquid water
Ice III
Ice V
Ice VII
Ice VI
Ice Ih
Ice II
Ice VIII
Ice XI
Temperature (K)
Pressure (GPa)
500
400
300
200
100
0
0.01
0.1
1
10


-200 °C
-100 °C
0 °C
100 °C
200 °C
300 °C
400 °C
500 °C
600 °C
700 °C
100 Mbar
10 Mbar
1 Mbar
100 kbar
10 kbar
1 kbar
100 bar
10 bar
1 bar
100 mbar
10 mbar
1 mbar
100 µbar
10 µbar
1 µbar
C2/m (metallic)
P2₁
Pbcm (XI)
X
VII
VIII
XV
XIII
IX
VI
V
III
II
1 TPa
1 GPa
1 MPa
1 kPa
1 Pa
Pressure
1 g.cm⁻³
Liquid
E
XI
Ic
Ih
Solid
Vapor
0
100
200
300
400
500
600
700
800
900
1000
Temperature (K)
(c)MPC

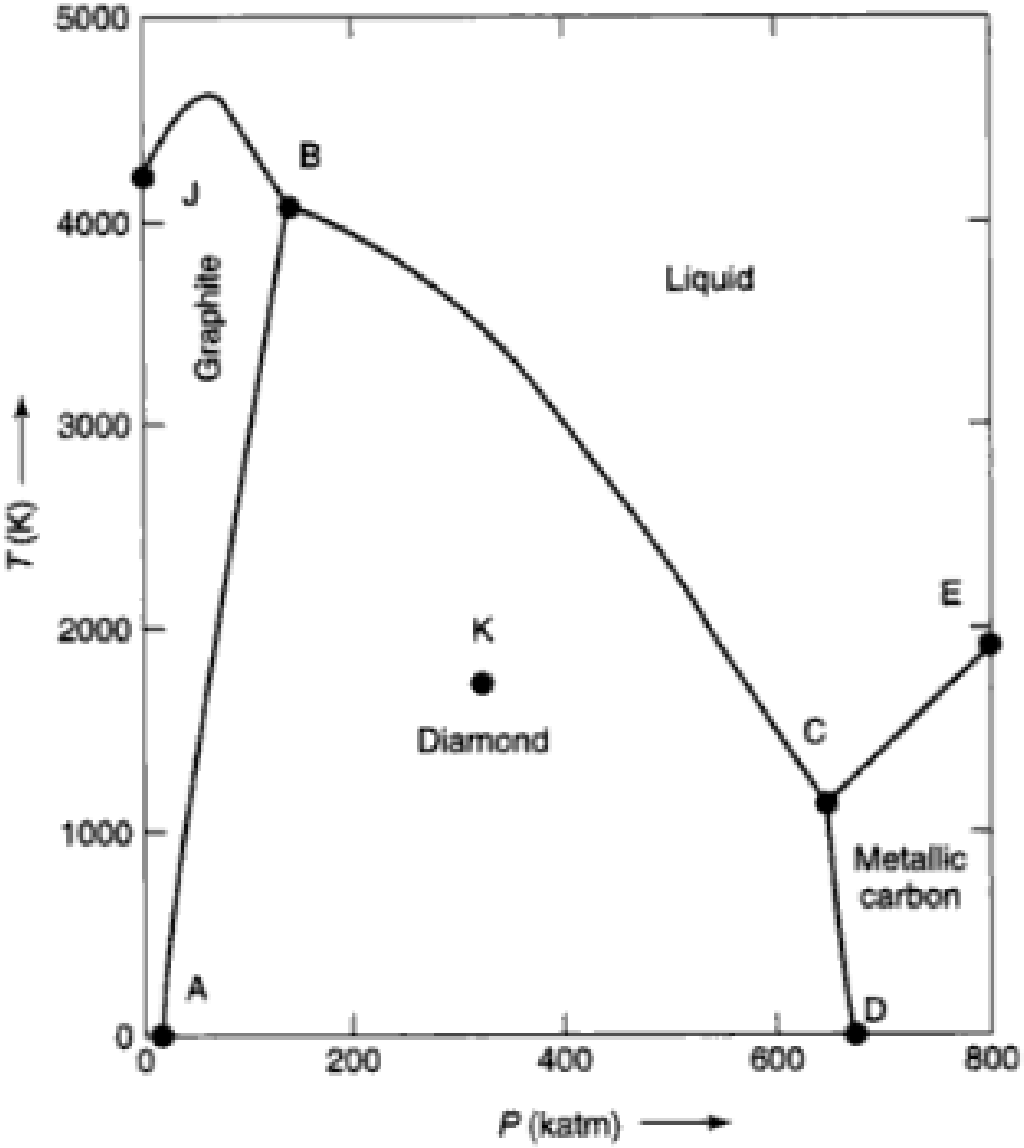


Figure 2.2 Temperature–Pressure unary phase diagram for carbon. From K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*. Copyright © 1976 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.

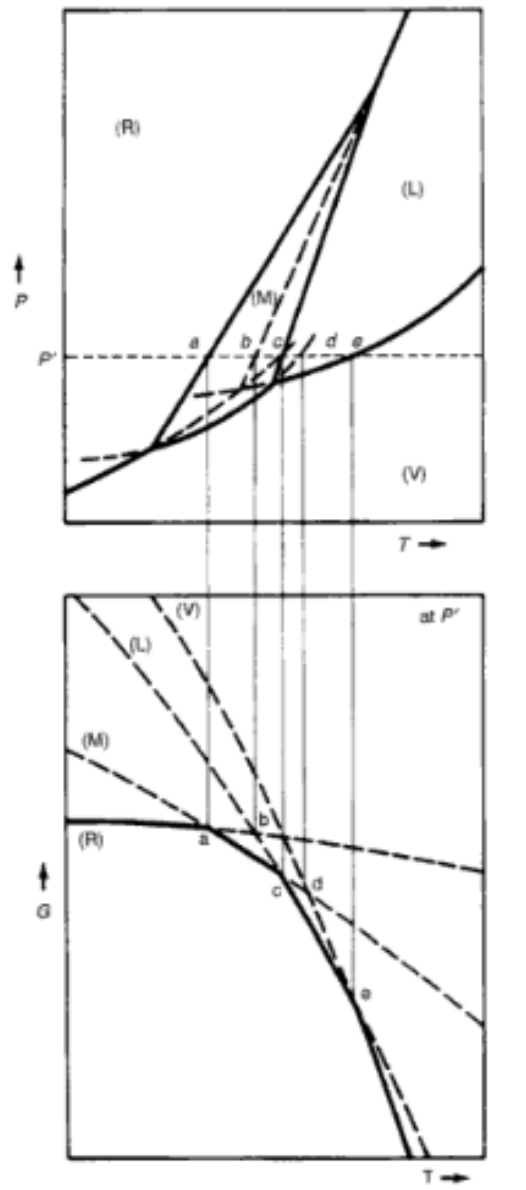


Figure 2.1 Unary phase diagram (*top*) and Gibbs free energy plot (*bottom*) for elemental sulfur. Reprinted, by permission, from D. R. Gaskell, *Introduction to Metallurgical Thermodynamics*, 2nd ed., p. 178, Copyright © 1981 by Hemisphere Publishing Corporation.

Binary Solid Solutions

$$G = H - TS$$

$$H = X_A H_A^\circ + X_B H_B^\circ + \Delta H_{mix}$$

$$S = X_A S_A^\circ + X_B S_B^\circ + \Delta S_{mix}$$

enthalpy and *entropy of mixing*

X_A and X_B are the mole fractions of component A and B.

$(X_A + X_B) = 1$

$$G = X_A(H_A^\circ - TS_A^\circ) + X_B(H_B^\circ - TS_B^\circ) + \Delta H_{mix} - T\Delta S_{mix}$$

$$G = X_A G_A^\circ + X_B G_B^\circ + \Delta G_{mix}$$

where $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

What exactly is ΔG_{mix}?

$$\Delta S_{conf} = \Delta S_{mix} = -R(X_A \ln X_A + X_B \ln X_B)$$

R is the gas constant

$$\Delta H_{mix} = \alpha X_A X_B$$

interaction energy, α

If $\alpha < 0$, *exothermic mixing* occurs ($\Delta H_{mix} < 0$)

Endothermic mixing ($\Delta H_{mix} > 0$)

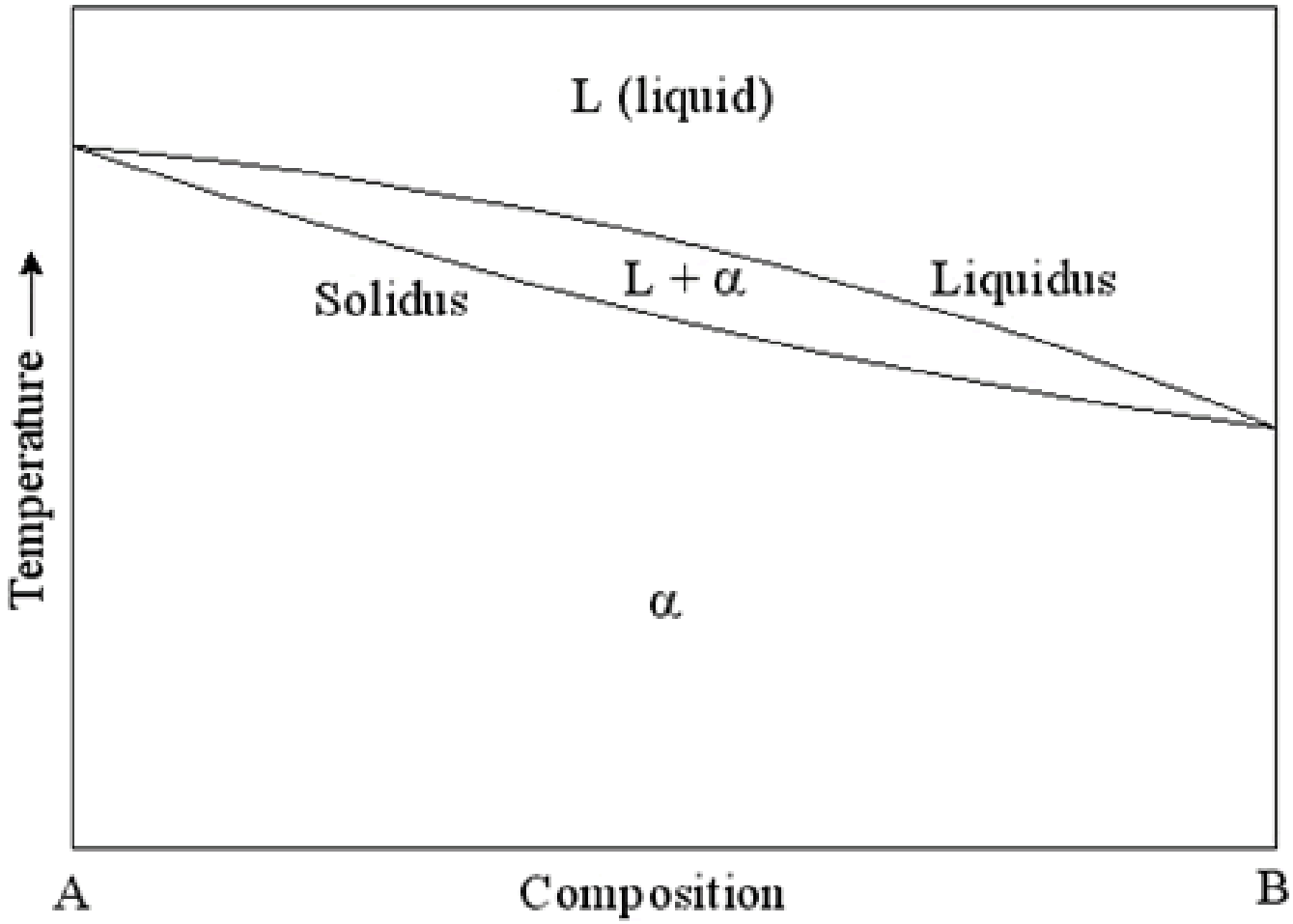
$$\alpha^{ideal} = \Delta H_{mix}^{ideal} = 0$$

$$\Delta G_{mix} = \alpha X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

$$G^{reg} = X_A G_A^\circ + X_B G_B^\circ + \alpha X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

Solutions whose free energies follow Eq. are said to be *regular*.

$$G^{ideal} = X_A G_A^\circ + X_B G_B^\circ + RT(X_A \ln X_A + X_B \ln X_B)$$



Schematic binary phase diagram showing miscibility in both the liquid and solid states.

www1.asminternational.org

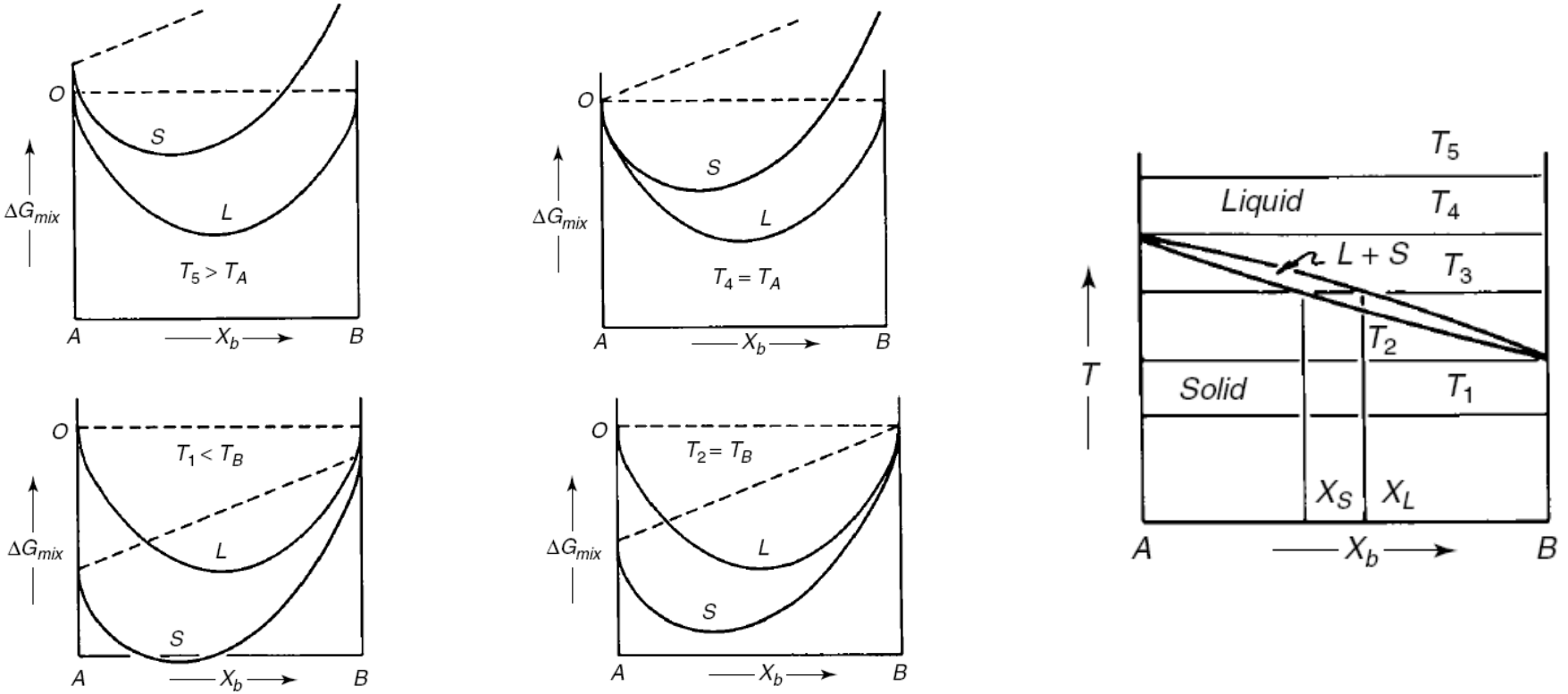


Figure 2.3 Free energy of mixing curves for solid and liquid phases at various temperatures (a–e) and resulting temperature–composition phase diagram for a completely soluble binary component system (f). From O. F. Devereux, *Topics in Metallurgical Thermodynamics*. Copyright © 1983 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.

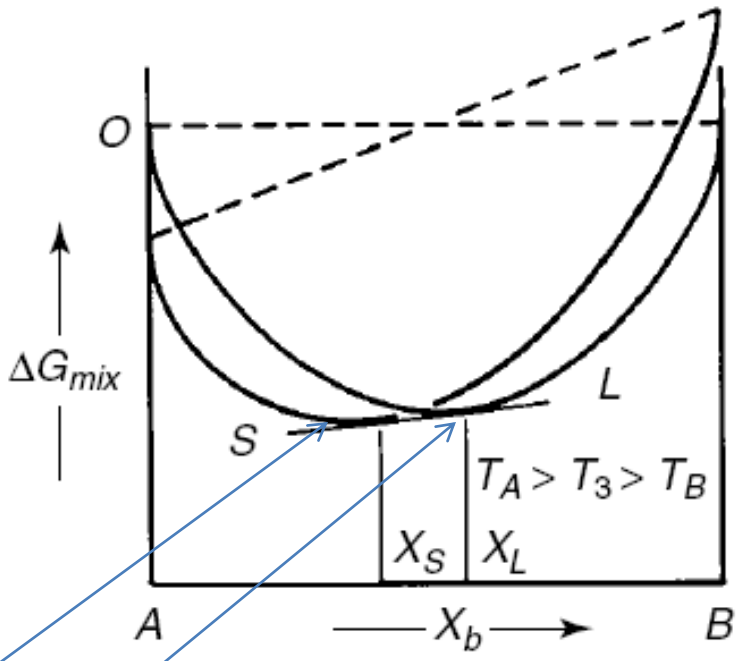
For 2 phase equilibrium

$$T_\alpha = T_\beta$$
$$P_\alpha = P_\beta$$
$$\mu_\alpha = \mu_\beta$$

Chemical potential $$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$$

Thus,

$$\mu_S = \left(\frac{\partial \Delta G_{mix,S}}{\partial X_B}\right)_{T,P,n_L} = \mu_L = \left(\frac{\partial \Delta G_{mix,L}}{\partial X_B}\right)_{T,P,n_S}$$

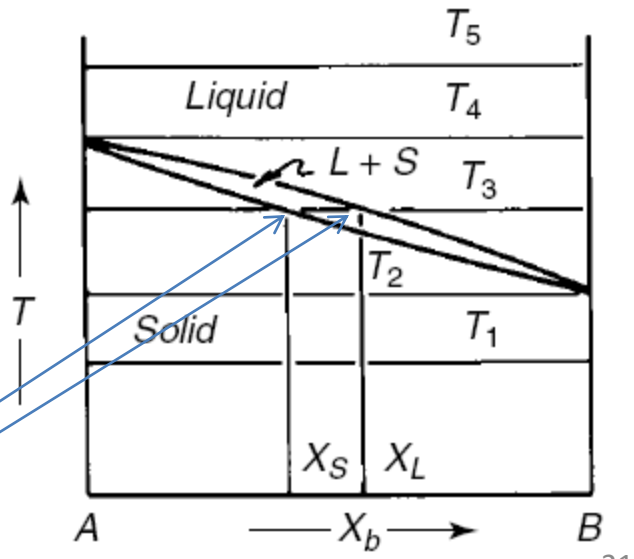


Graphically, this is true for the common tangent to the two curves

Also, $$\left(\frac{\partial^2 \Delta G_{mix,S}}{\partial X_B^2}\right) = 0$$

$$\left(\frac{\partial^2 \Delta G_{mix,L}}{\partial X_B^2}\right) = 0$$

give the minima to each curve



Plotting for various temperatures,

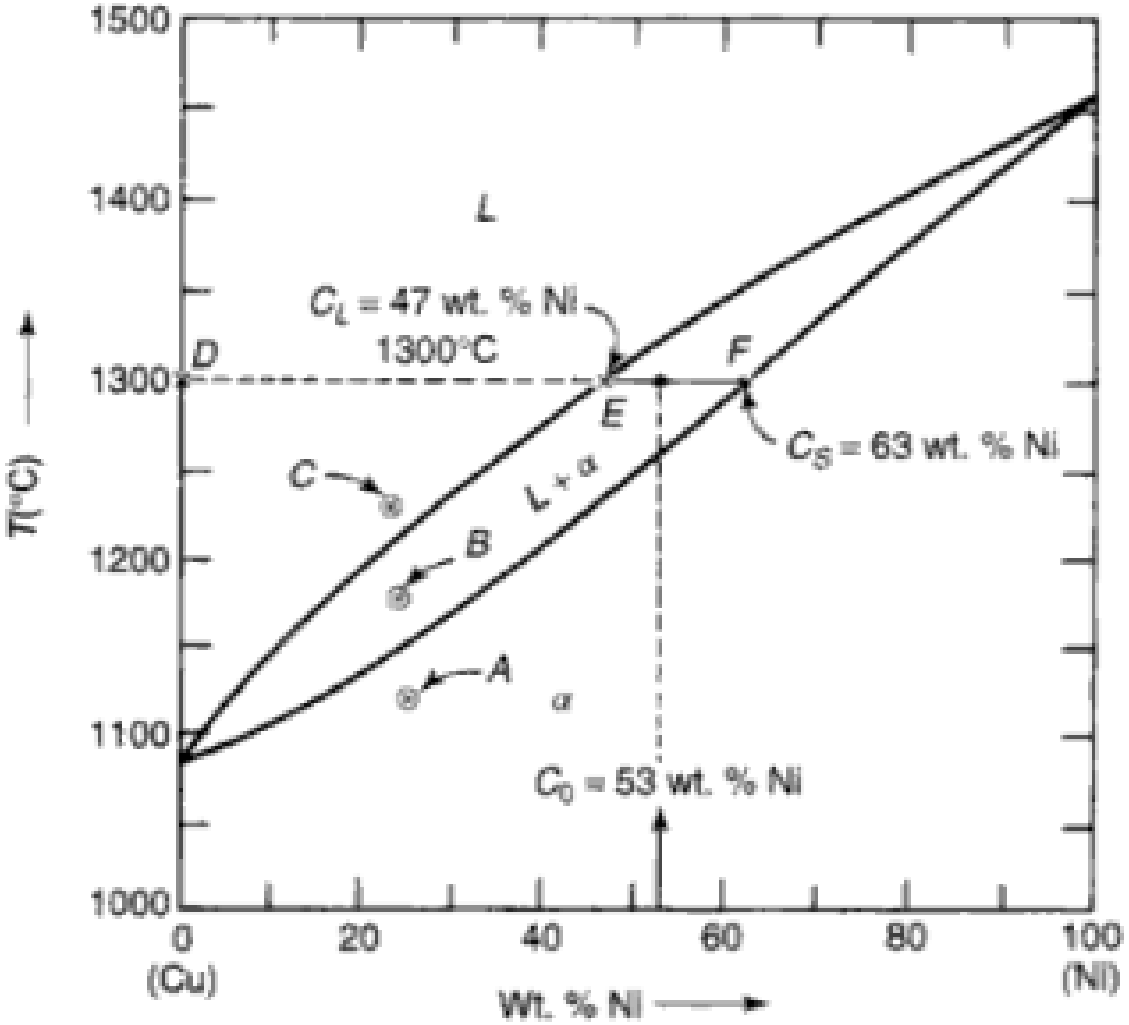


Figure 2.4 The Cu–Ni phase diagram, illustrating the use of the lever rule. From K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*. Copyright © 1976 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.

LEVER RULE

$$W_S + W_L = 1$$

$$W_S C_s + W_L C_L = C_o$$

$$W_L = \frac{C_o - C_S}{C_s - C_L}$$

$$W_S = \frac{C_L - C_O}{C_s - C_L}$$

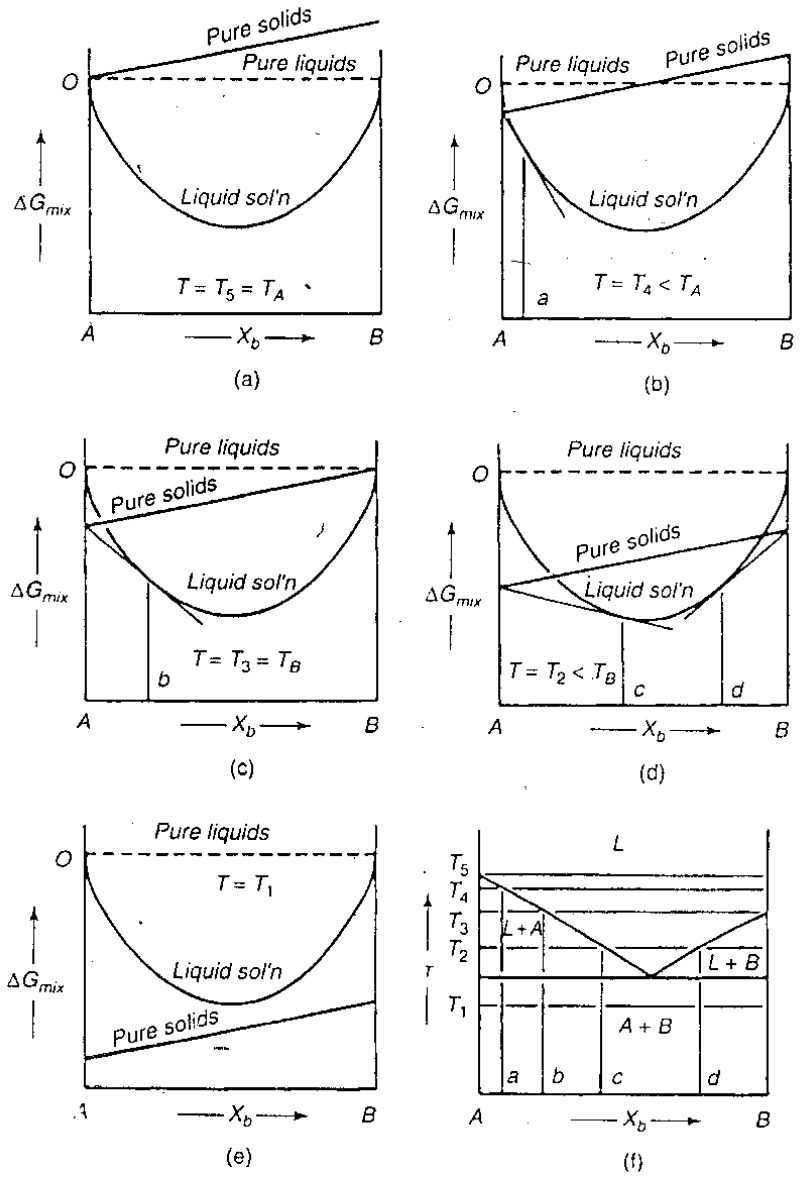


Figure 2.5 Free energy of mixing for solid and liquid phases at various temperatures (a–e) and resulting temperature–composition phase diagram for a slightly soluble eutectic binary component system (f). From O. F. Devereux, *Topics in Metallurgical Thermodynamics*. Copyright © 1983 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.

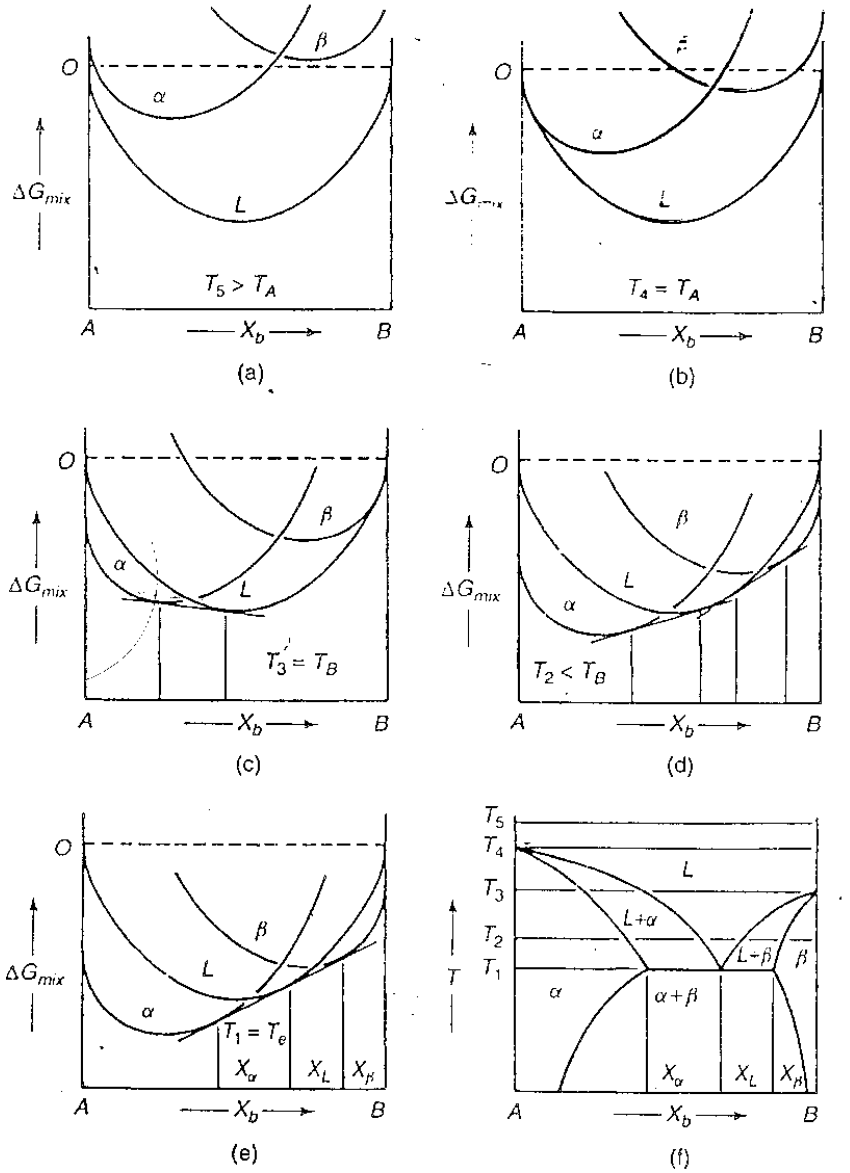
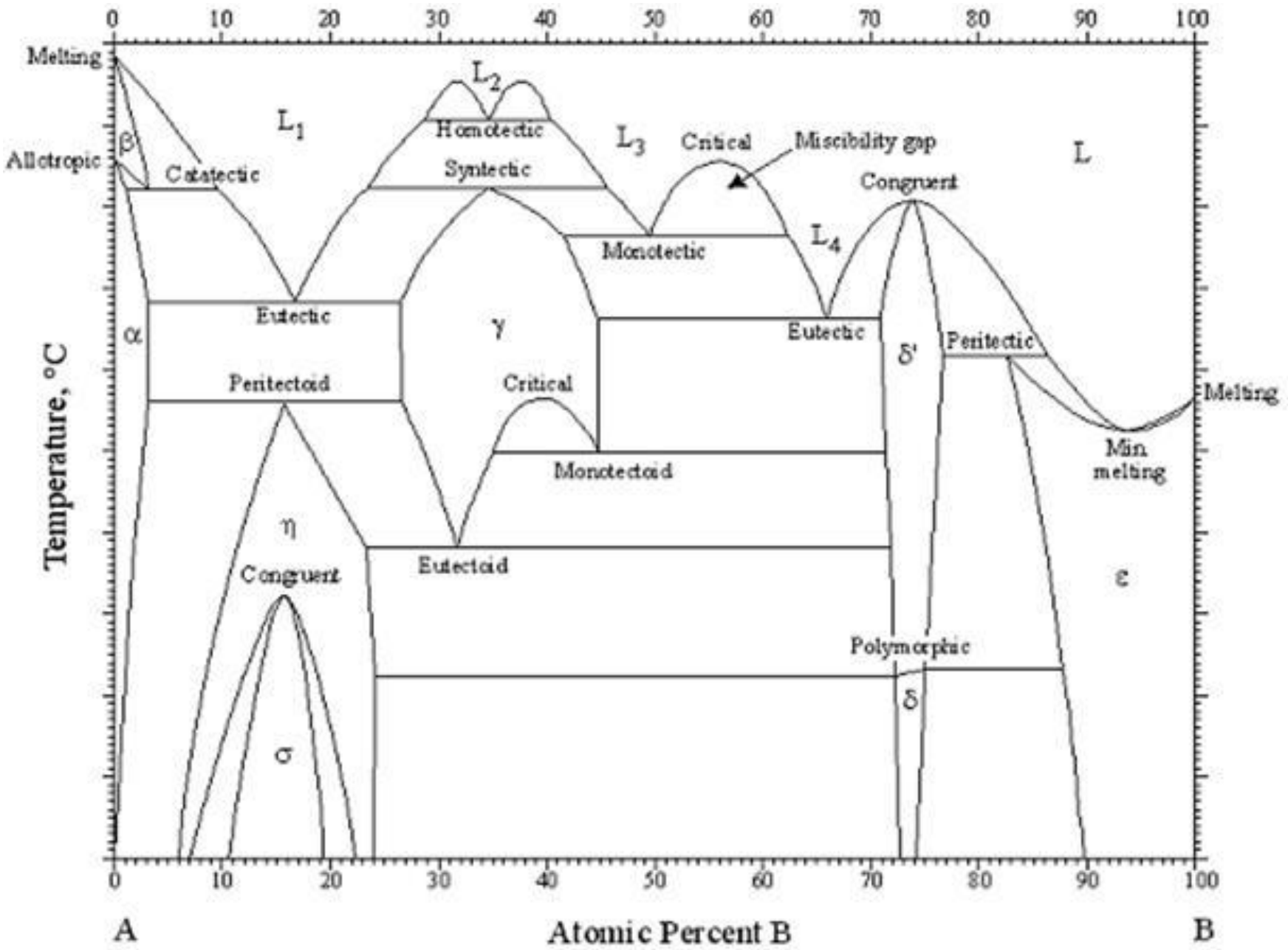


Figure 2.6 Free energy of mixing for solid and liquid phases at various temperatures (a–e) and resulting temperature–composition phase diagram for a mostly insoluble binary component system (f). From O. F. Devereux, *Topics in Metallurgical Thermodynamics*. Copyright © 1983 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.

Table 2.3 Common Three-phase Transformations in Condensed Binary Systems

Name of Reaction	Equation	Phase Diagram Characteristic
Monotectic	$L_I \xrightarrow{\text{cooling}} \alpha + L_{II}$	
Monotectoid	$\alpha_1 \xrightarrow{\text{cooling}} \alpha_2 + \beta$	
Eutectic	$L \xrightarrow{\text{cooling}} \alpha + \beta$	
Eutectoid	$\alpha \xrightarrow{\text{cooling}} \beta + \gamma$	
Syntectic	$L_I + L_{II} \xrightarrow{\text{cooling}} \alpha$	
Peritectic	$\alpha + L \xrightarrow{\text{cooling}} \beta$	
Peritectoid	$\alpha + \beta \xrightarrow{\text{cooling}} \gamma$	

Source: K. M. Ralls, T. H. Courtney and J. Wulff, *Introduction to Materials Science and Engineering*, p. 331.


0
10
20
30
40
50
60
70
80
90
100
Melting
Allotropic
β
Catatectic
L1
L2
Monotectic
Syntectic
L3
Critical
Miscibility gap
L
Congruent
L4
Monotectic
α
Eutectic
γ
Eutectic
δ'
Peritectic
Peritectoid
Critical
Melting
Monotectoid
Min melting
η
Congruent
Eutectoid
ε
Polymorphic
δ
σ
Temperature, °C
A
Atomic Percent B
B

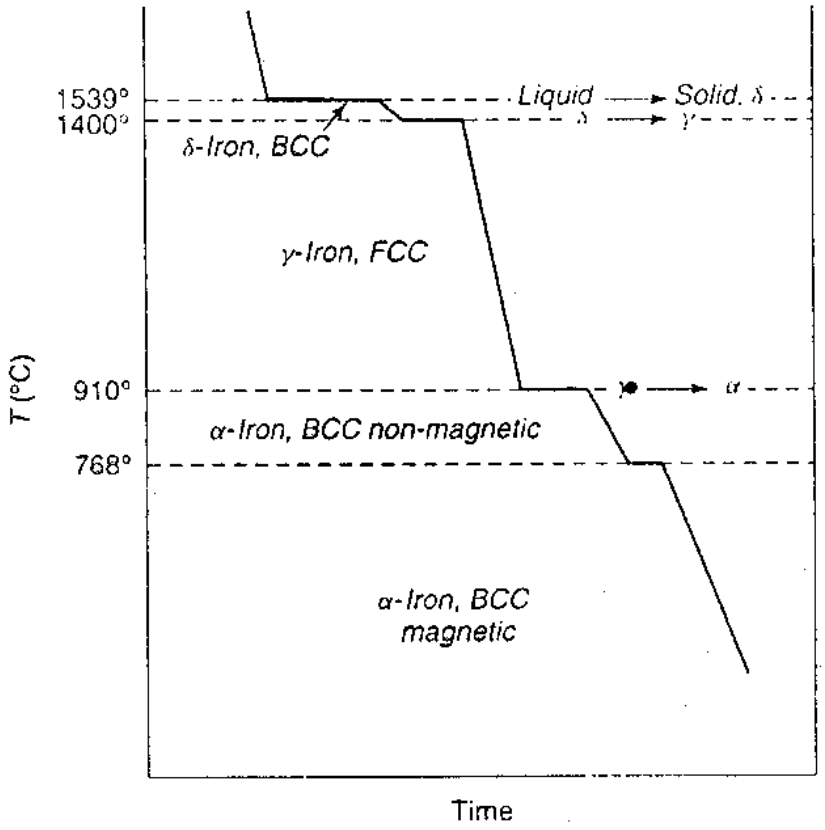


Figure 2.9 Cooling curve for pure iron. Reprinted, by permission, from Committee on Metallurgy, *Engineering Metallurgy*, p. 245. Copyright © 1957 by Pitman Publishing.

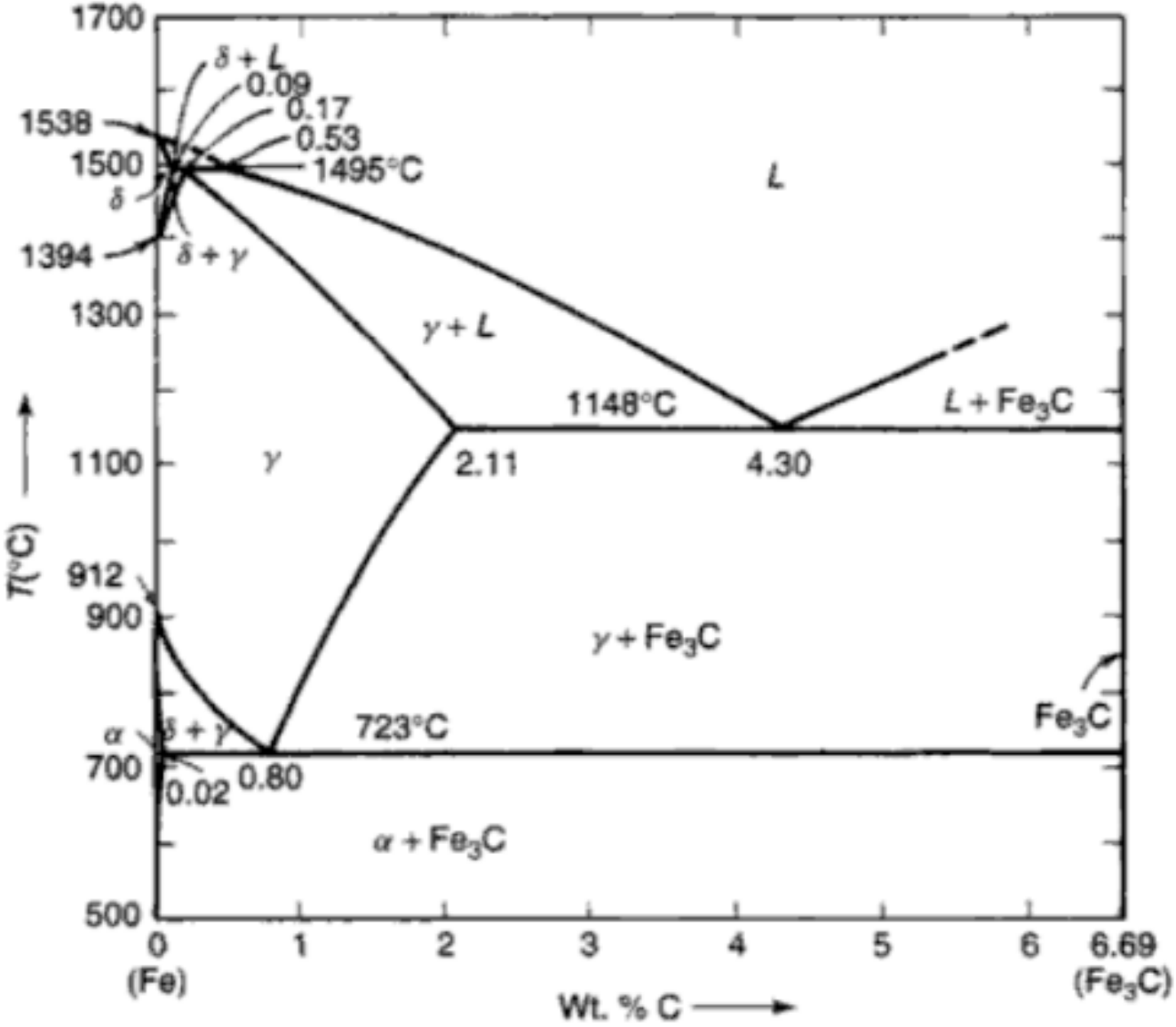


Figure 2.8 The Fe–C phase diagram (low weight % C). From K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*. Copyright © 1976 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.

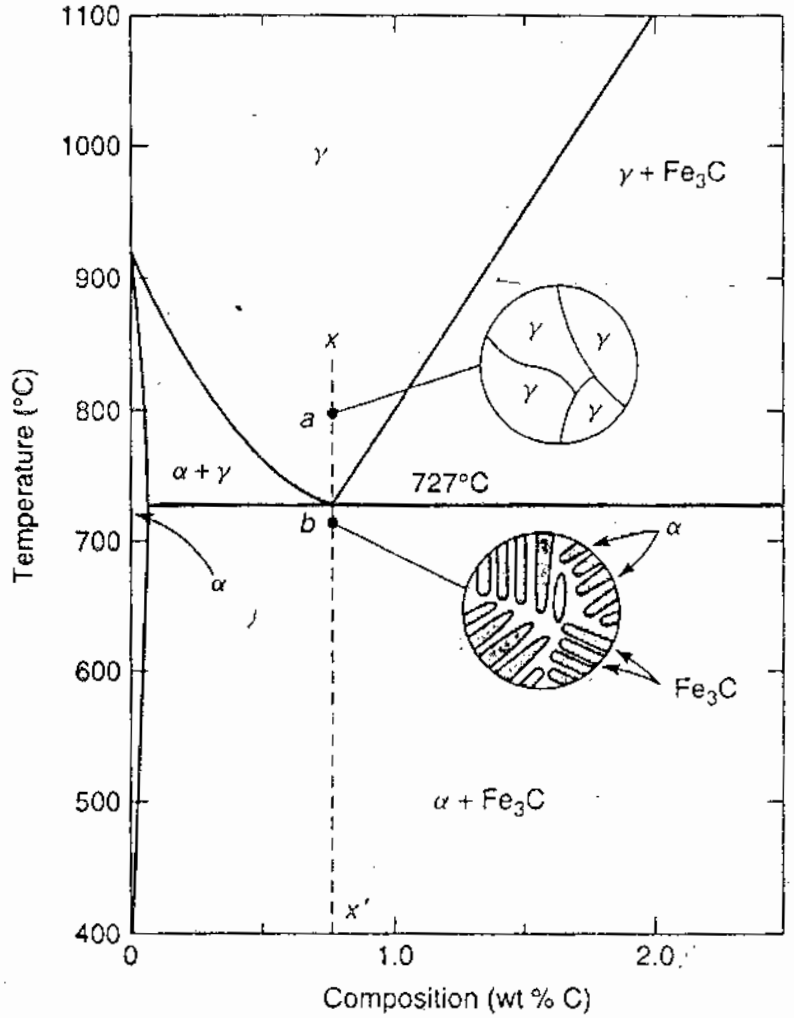


Figure 2.10 Schematic representation of the microstructures for a eutectoid transformation in the Fe–C system. Reprinted, by permission, from W. Callister, *Materials Science and Engineering: An Introduction*, 5th ed., p. 277. Copyright © 2000 by John Wiley & Sons, Inc.

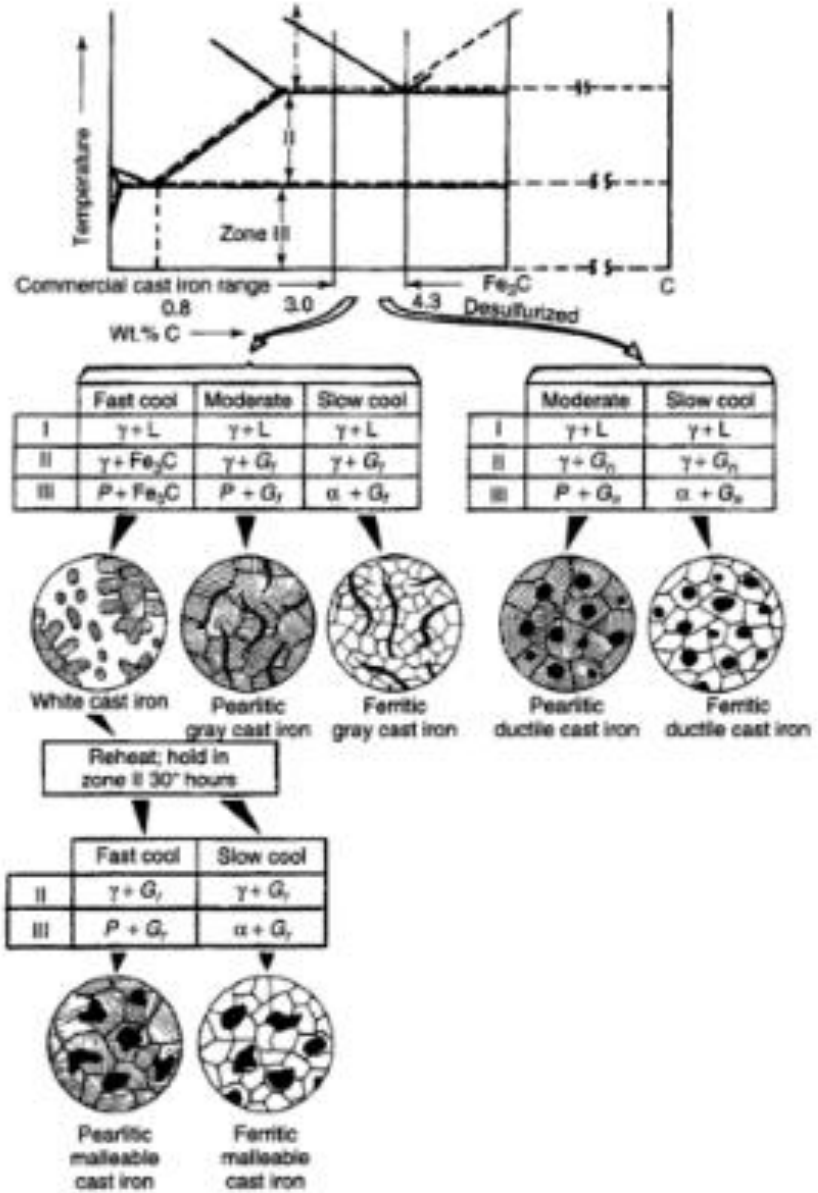


Figure 2.13 Microstructures obtained by varying thermal treatments in cast irons (G_f = graphite flakes; G_r = graphite rosettes; G_n = graphite nodules; P = pearlite). From K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*. Copyright © 1976 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.

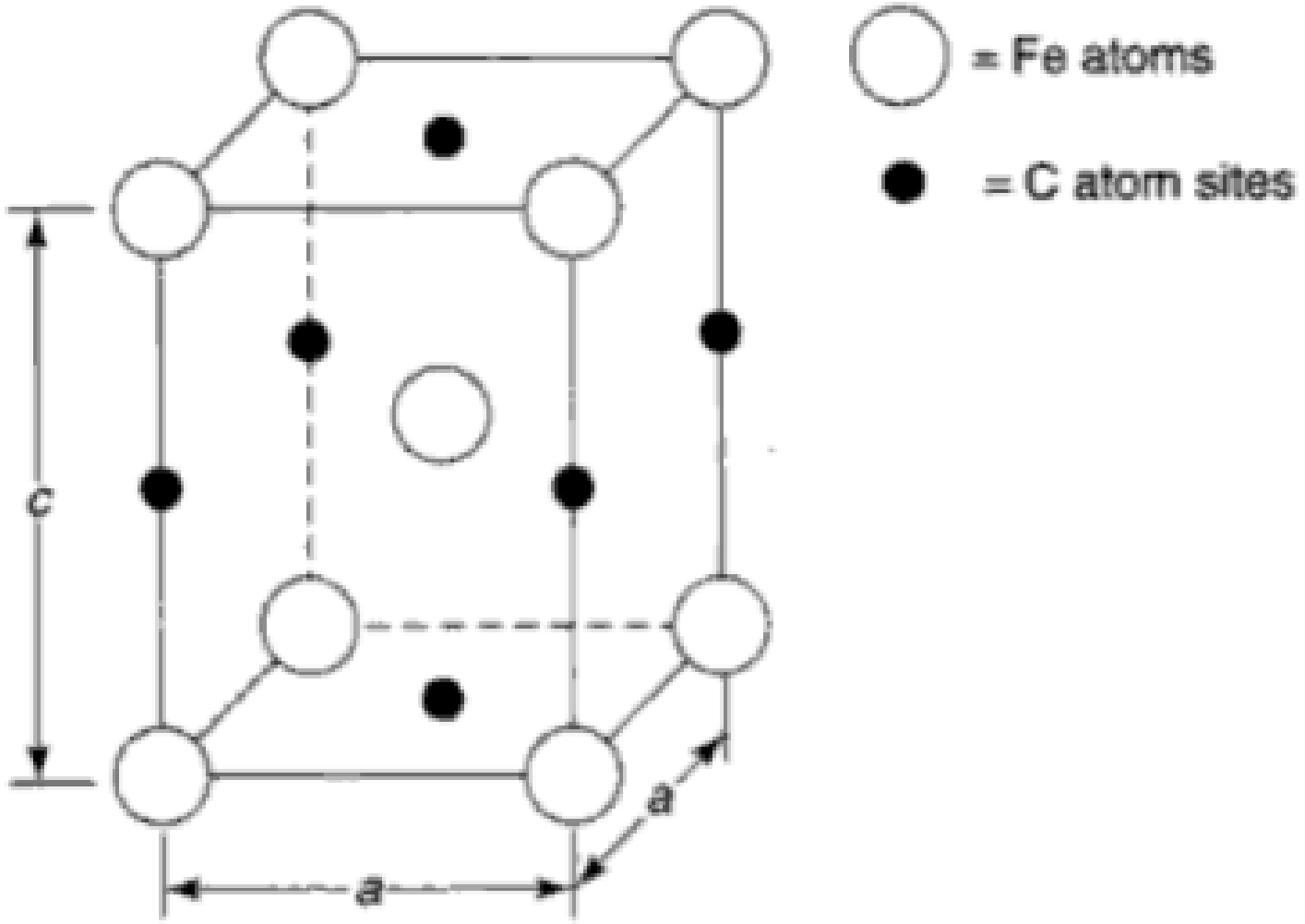


Figure 2.11 The body-centered tetragonal unit cell of steel martensite. From K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*. Copyright © 1976 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.

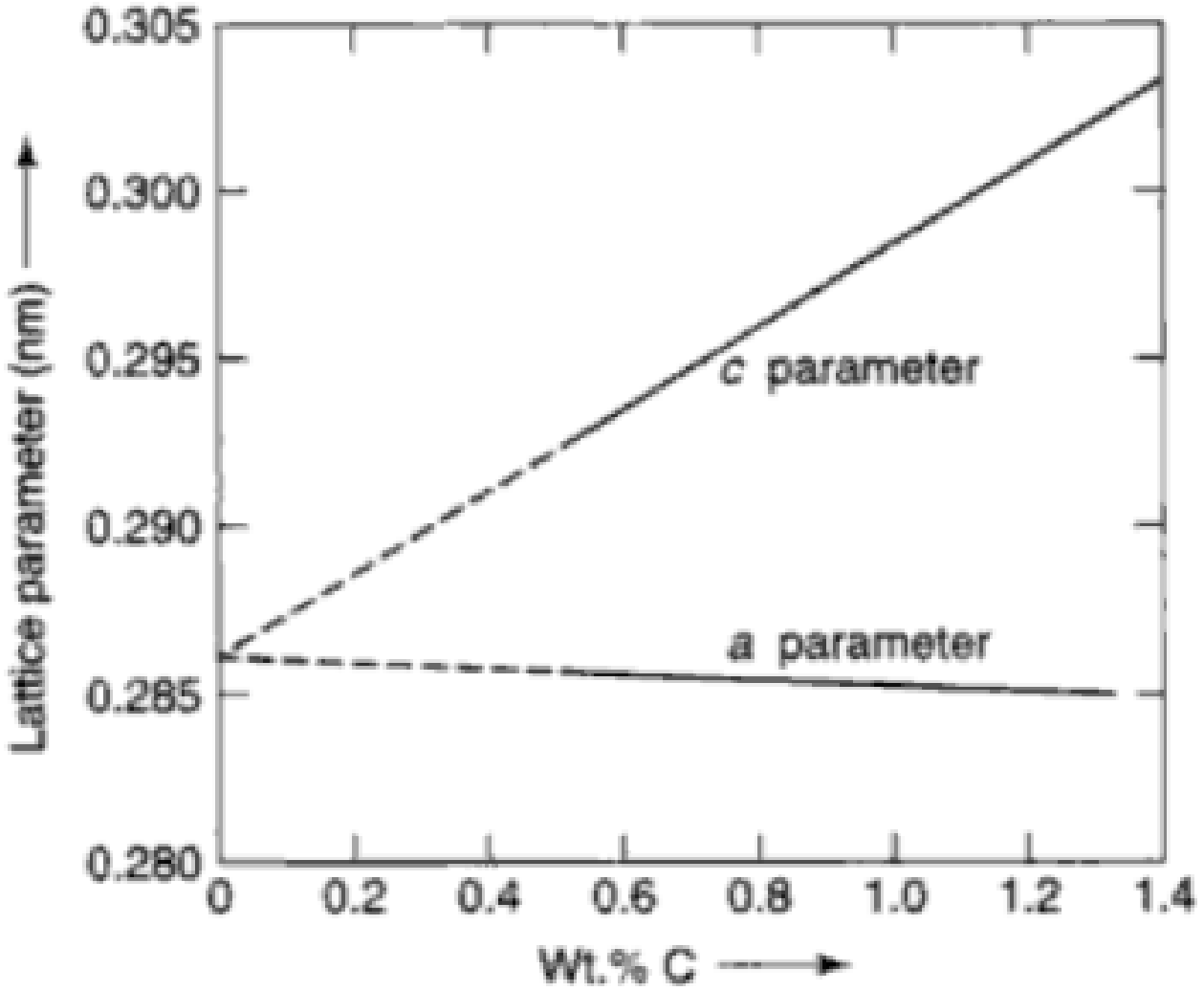
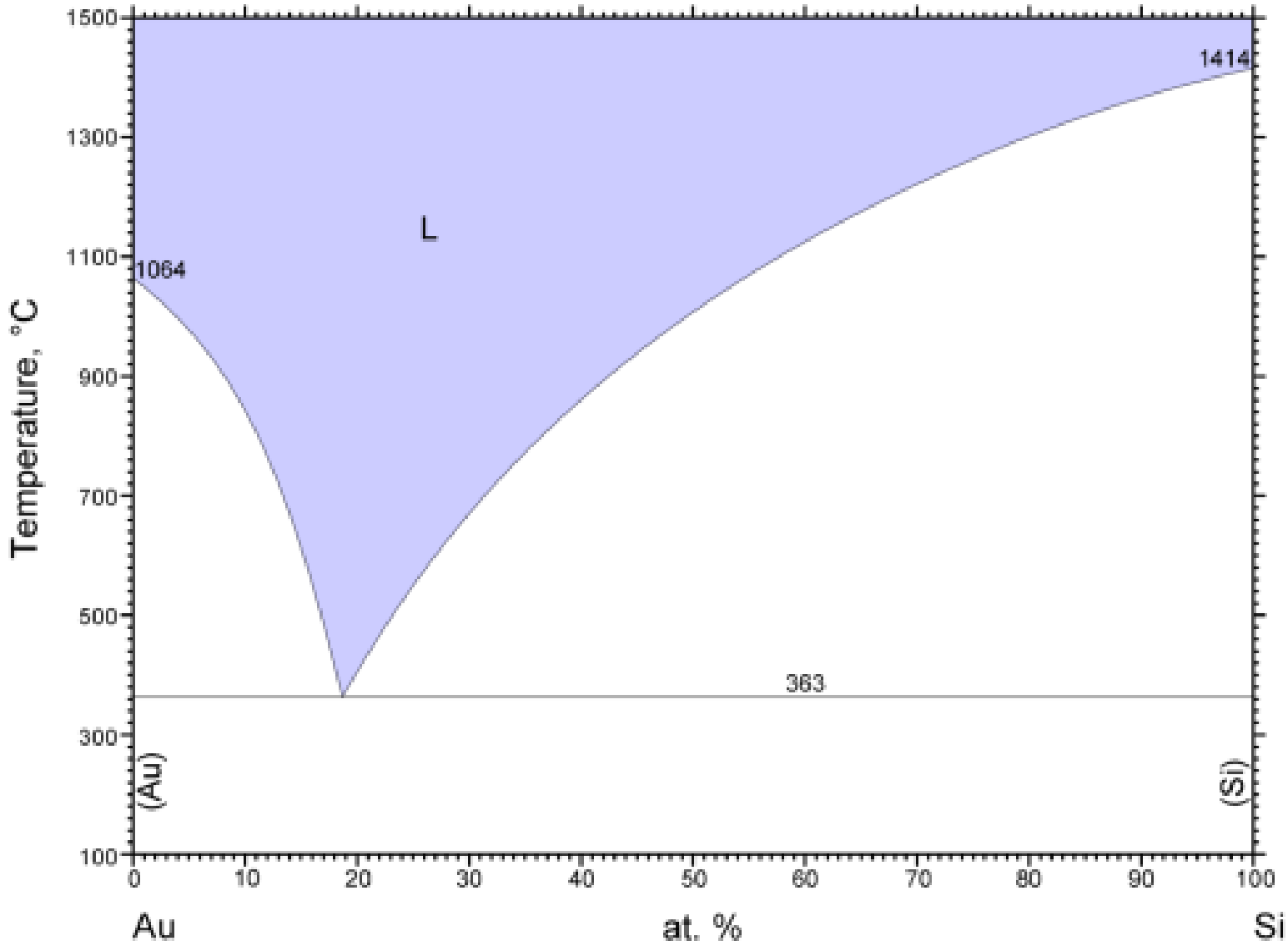
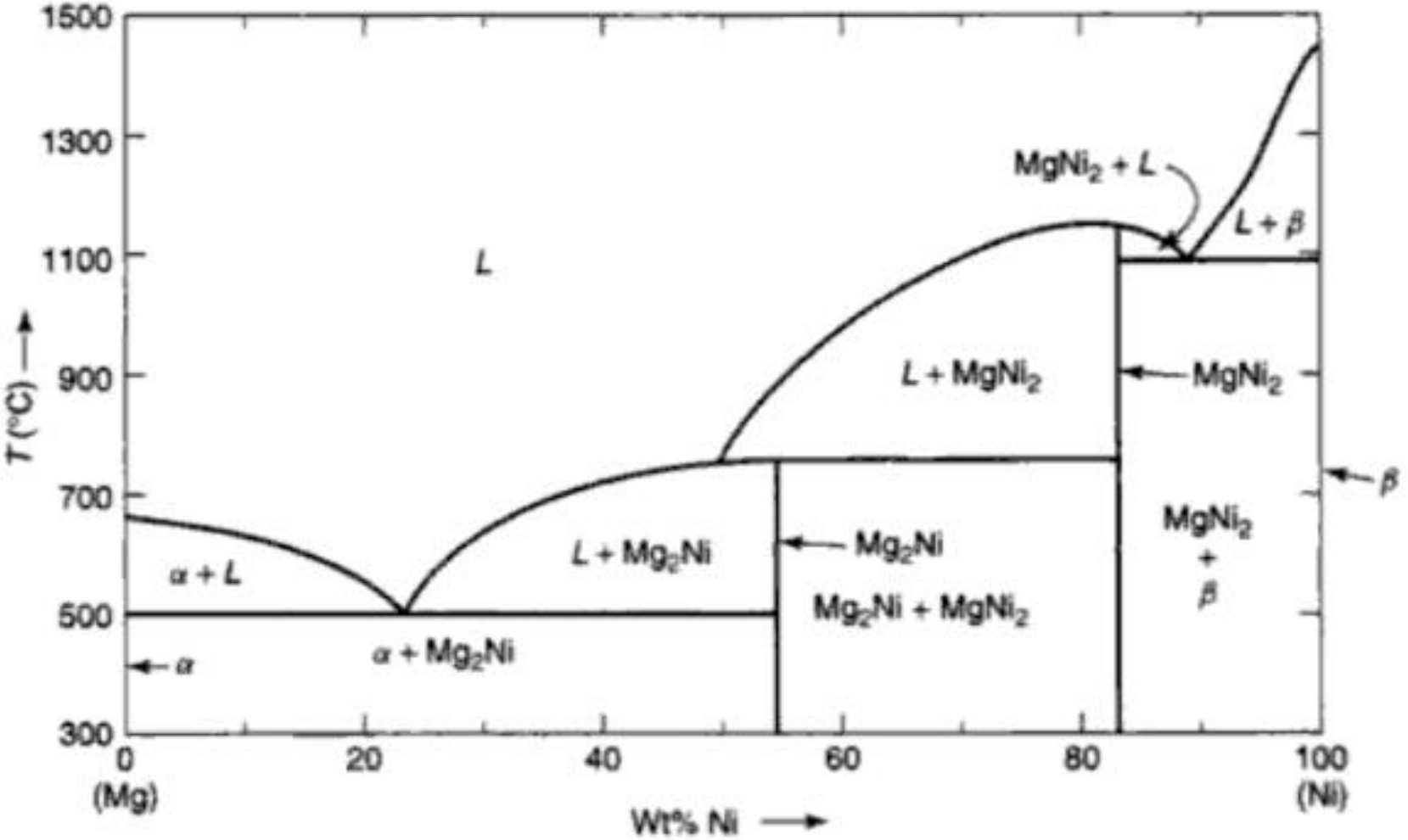


Figure 2.12 Variation of tetragonality in steel martensite with axial ratio. From K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*. Copyright © 1976 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.


1500
1300
1100
900
700
500
300
100
Temperature, °C
L
1064
1414
363
(Au)
(Si)
0
10
20
30
40
50
60
70
80
90
100
Au
at. %
Si



Reprinted, by permission, from K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*, p. 333. Copyright © 1976 by John Wiley & Sons, Inc.

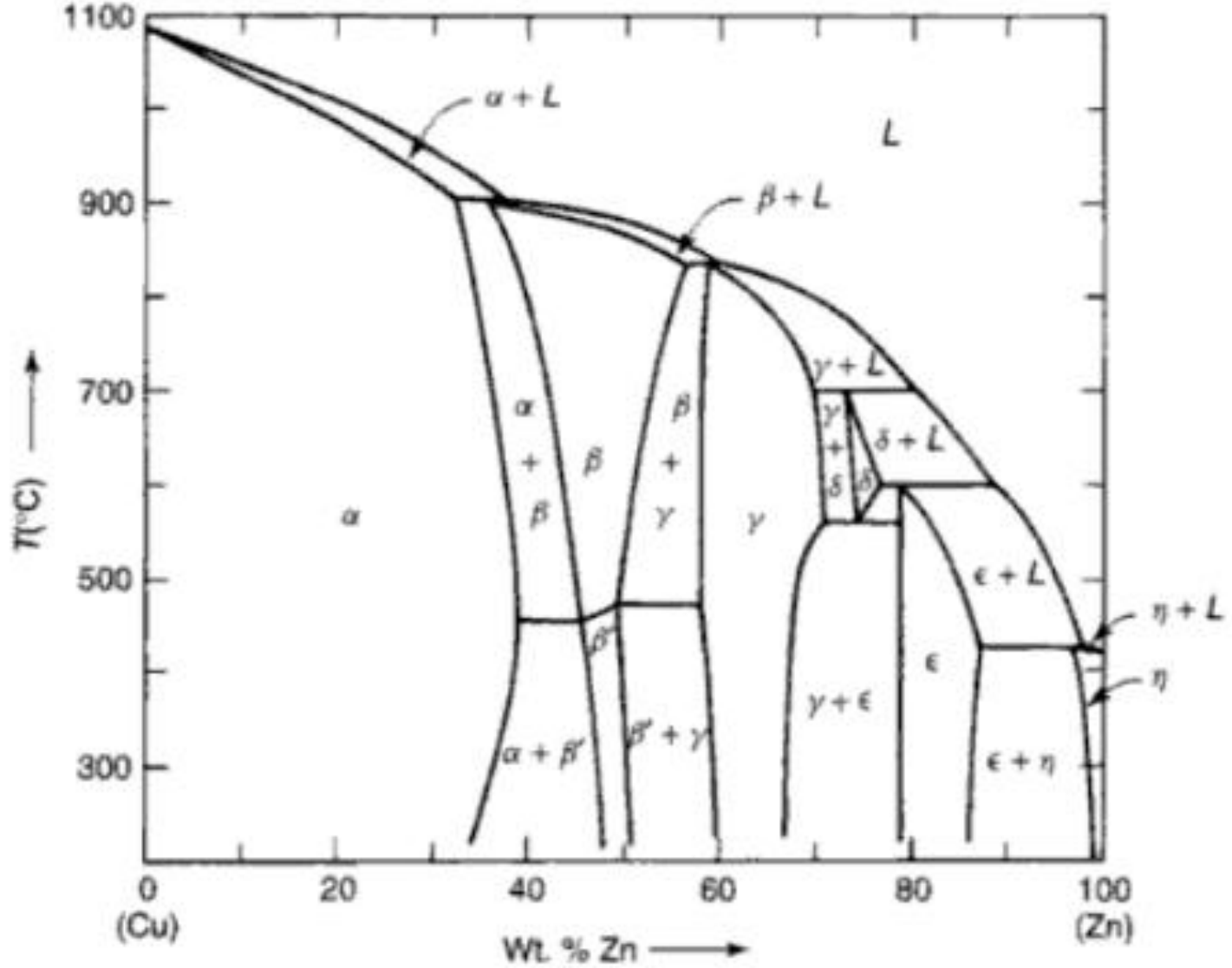
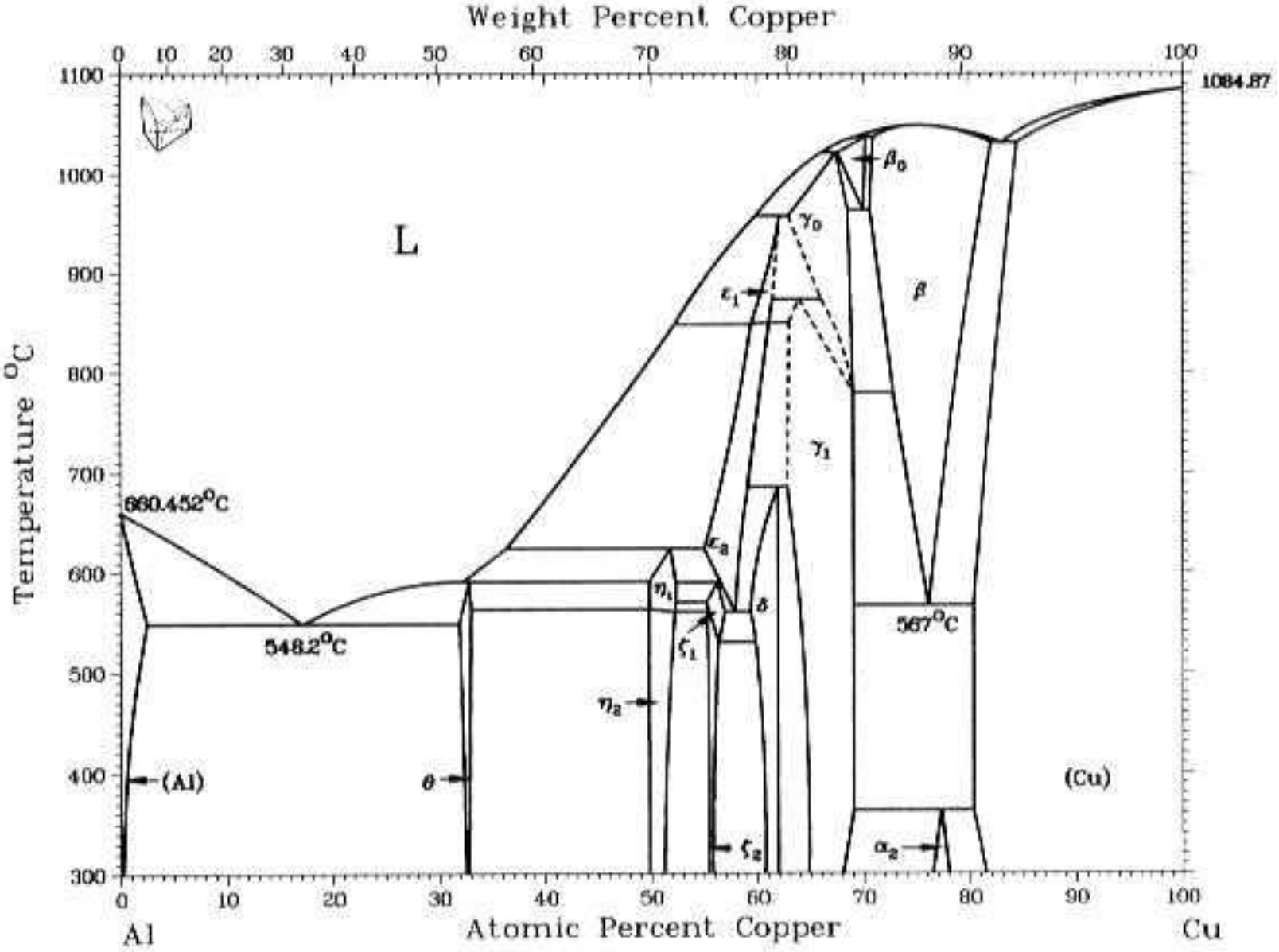


Figure 2.7 Cu–Zn phase diagram, illustrating a number of three-phase reactions. From K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*. Copyright © 1976 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.


Weight Percent Copper
0 10 20 30 40 50 60 70 80 90 100
1100
1000
900
800
700
600
500
400
300
Temperature °C
L
1084.87
660.452°C
548.2°C
567°C
(Al)
(Cu)
θ
β0
γ0
ε1
β
γ1
ε2
η1
δ
ζ1
η2
ζ2
α2
0 10 20 30 40 50 60 70 80 90 100
Al
Atomic Percent Copper
Cu

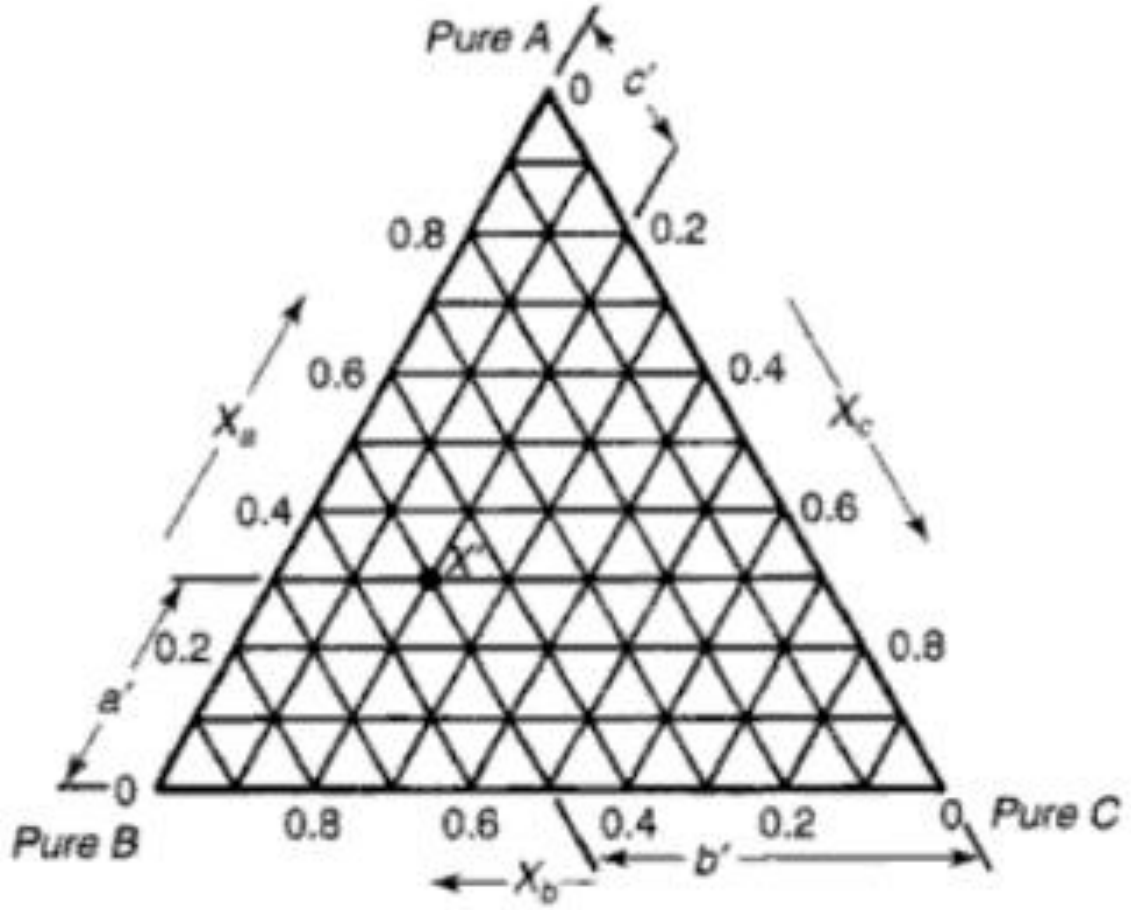


Figure 2.14 Illustration of how to express compositions on a three-component diagram. From O. F. Devereux, *Topics in Metallurgical Thermodynamics*. Copyright © 1983 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.

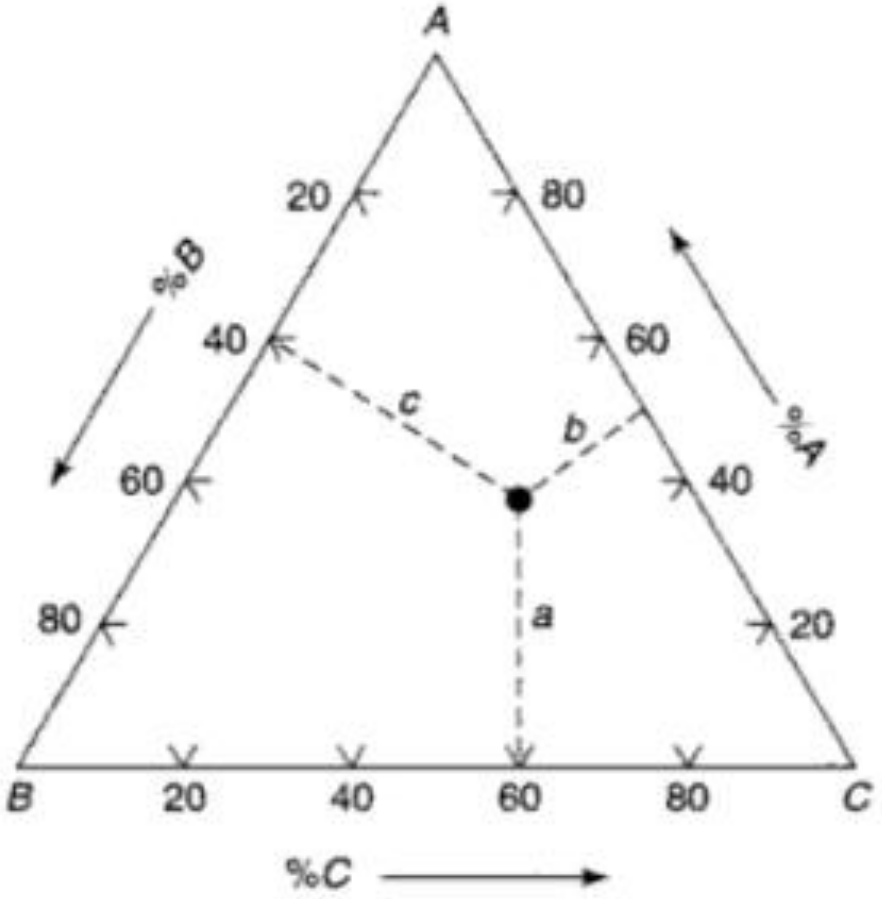


Figure 2.15 Illustration of center-of-gravity rule for determining compositions in ternary system.

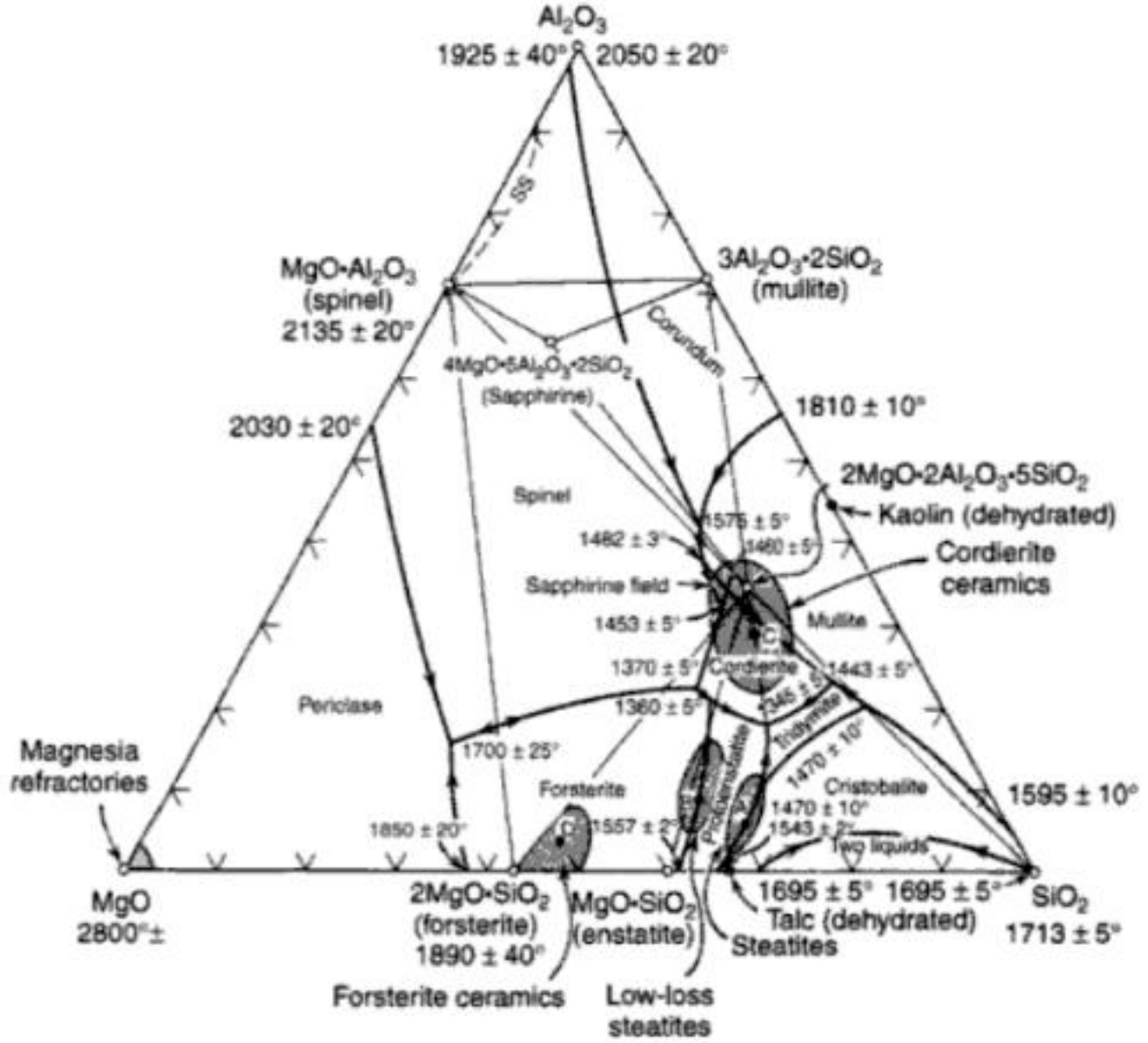
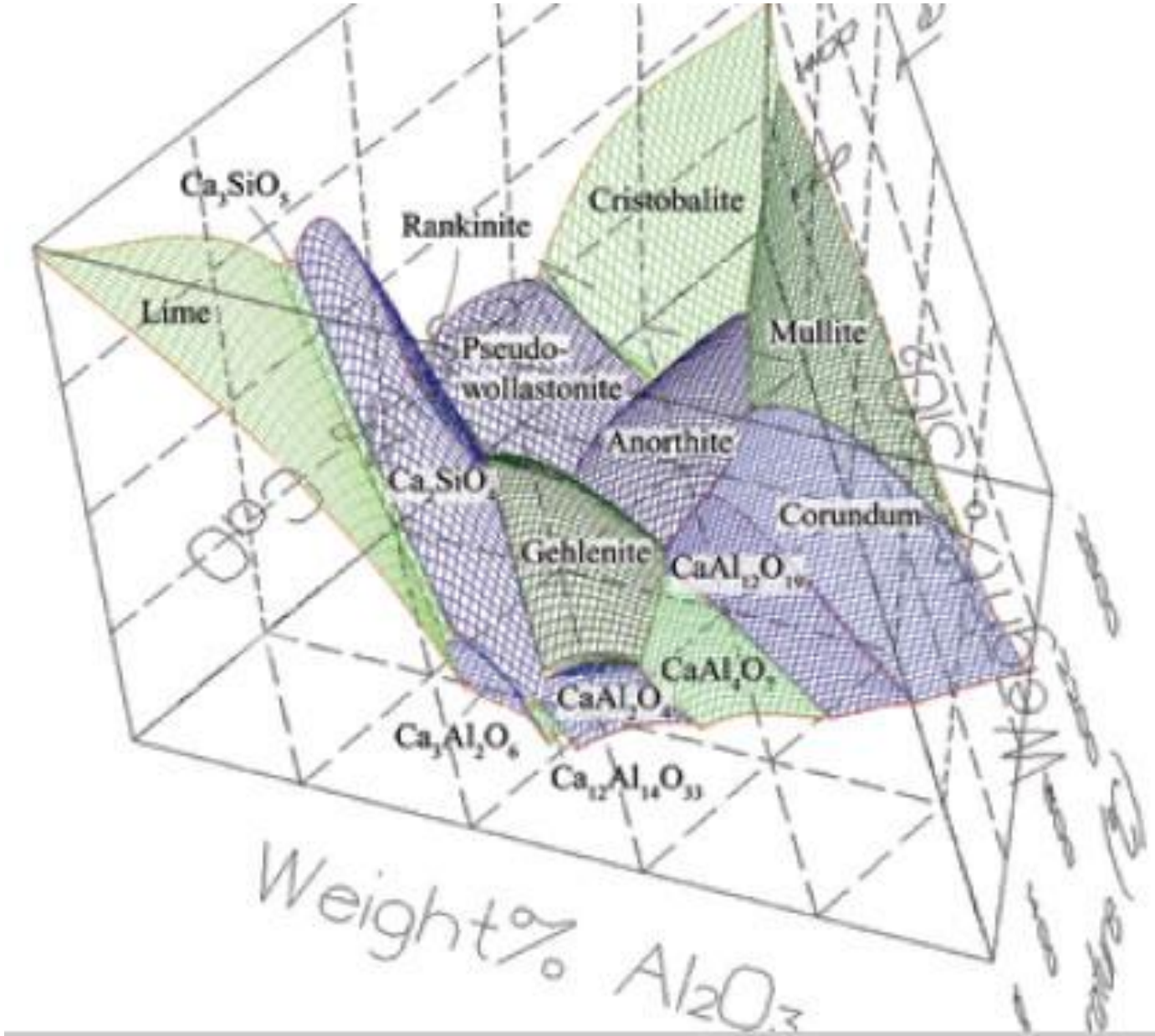


Figure 2.23 The $MgO-Al_2O_3-SiO_2$ phase diagram. Temperatures are in °C. From *Introduction to Ceramics*. W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, Copyright © 1976 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.



3-point perspective rendering of the CaO-Al2O3-SiO2 system.

www.mse.gatech.edu

SURFACE ENERGY

(Surface Tension in liquids)

$$dW_S = \gamma dA$$

$$\gamma = \frac{dW_S}{dA}$$

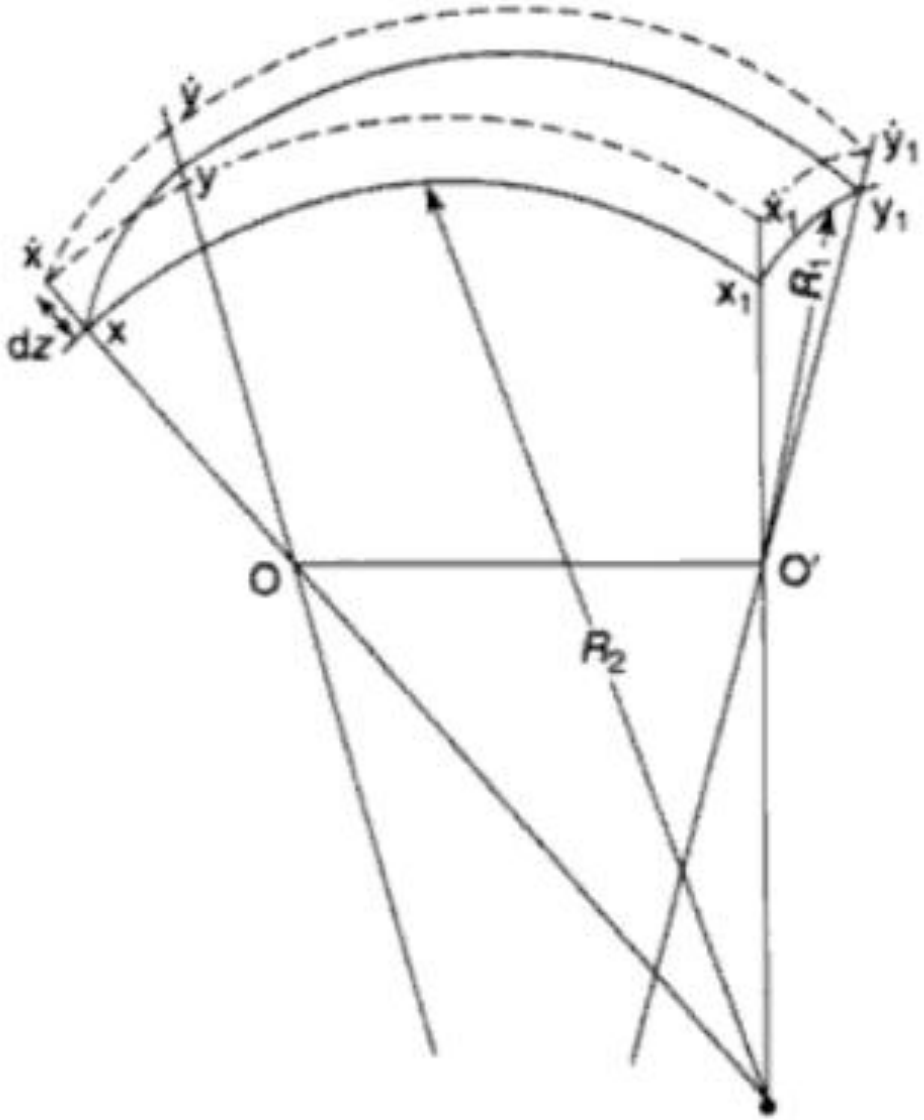


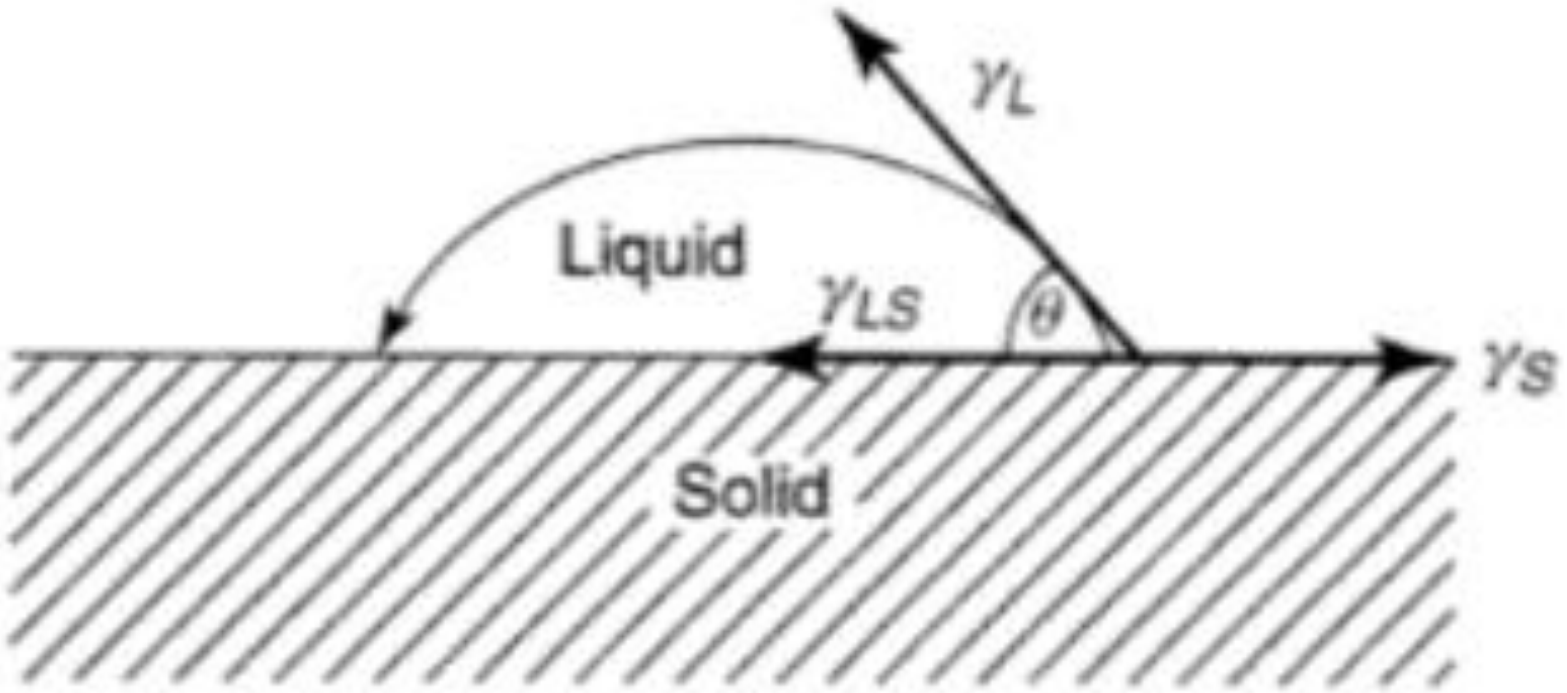
Figure 2.28 An element of a curved surface with principal radii R_1 and R_2. Reprinted, by permission, from J. F. Padday, in *Surface and Colloid Science*, E. Matijevic, ed., Vol. 1, p. 79. Copyright © 1969 by John Wiley & Sons, Inc.

LaPlace Equation

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

$$\Delta P = \frac{2\gamma}{R}$$

$$\Delta P = 0$$



$$\gamma_L \cos\theta + \gamma_{SL} = \gamma_S$$ (Young's Equation 1805)

Figure 2.29 Schematic diagram of liquid droplet on solid surface. From Z. Jastrzebski, *The Nature and Properties of Engineering Materials*, 2nd ed., Copyright © 1976 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.

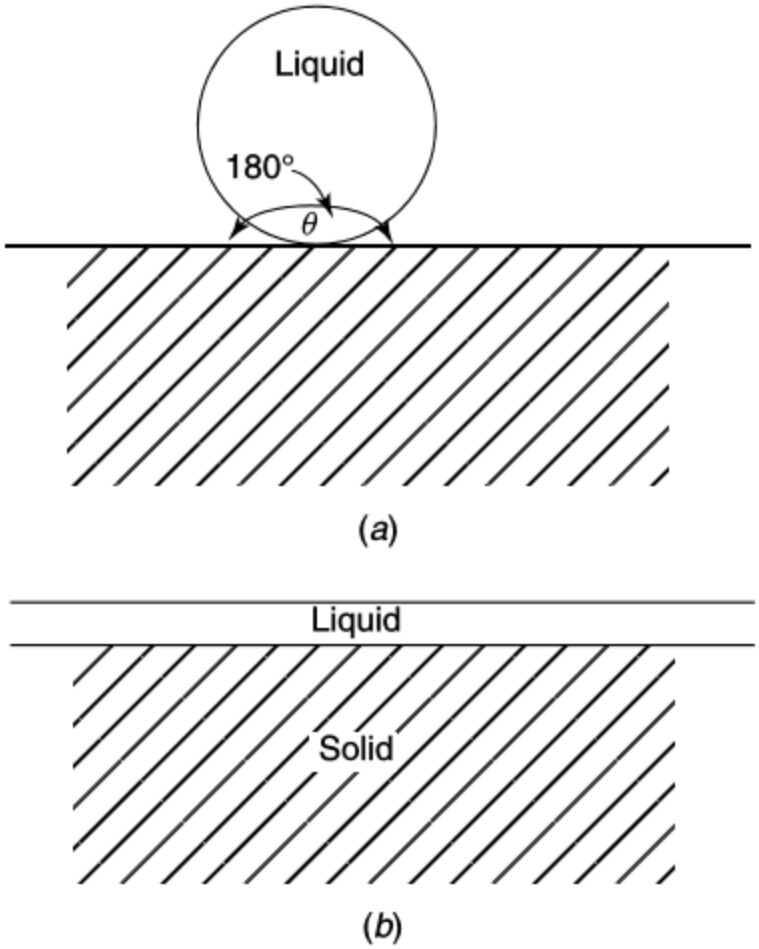


Figure 2.30 Schematic illustration of (a) nonwetting and (b) wetting of a liquid on a solid. From Z. Jastrzebski, *The Nature and Properties of Engineering Materials*, 2nd ed., Copyright © 1976 by John Wiley & Sons, Inc. This material is used by permission of John Wiley & Sons, Inc.

SINTERING

$$\Delta G = \Delta G_V + \Delta G_b + \Delta G_S$$

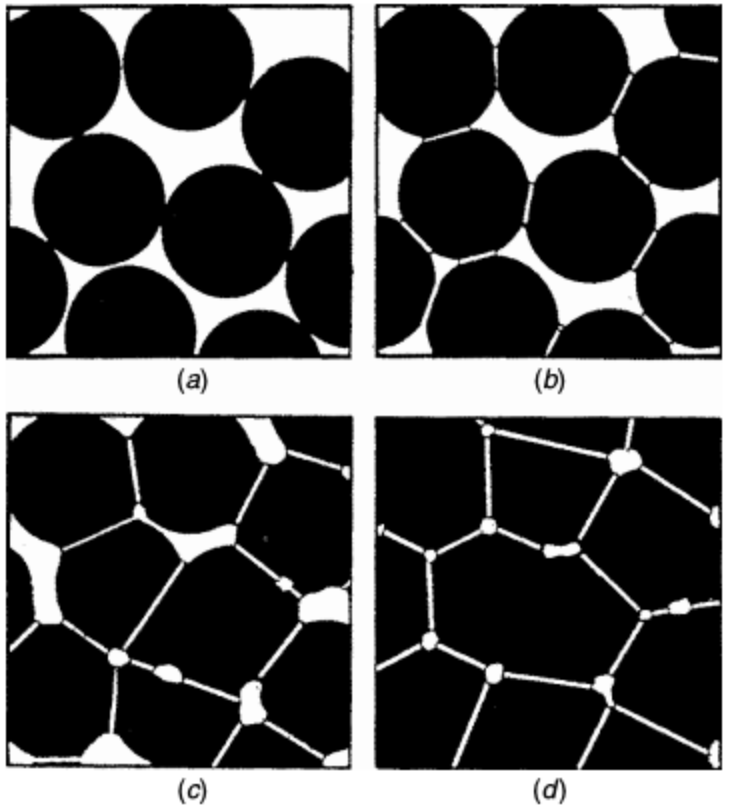


Figure 2.31 Development of ceramic microstructure during sintering: (a) Loose powder particles; (b) initial stage; (c) intermediate stage; and (d) final stage. From W. E. Lee and W. M. Rainforth, *Ceramic Microstructures*, p. 37. Copyright © 1994 by William E. Lee and W. Mark Rainforth, with kind permission of Kluwer Academic Publishers.

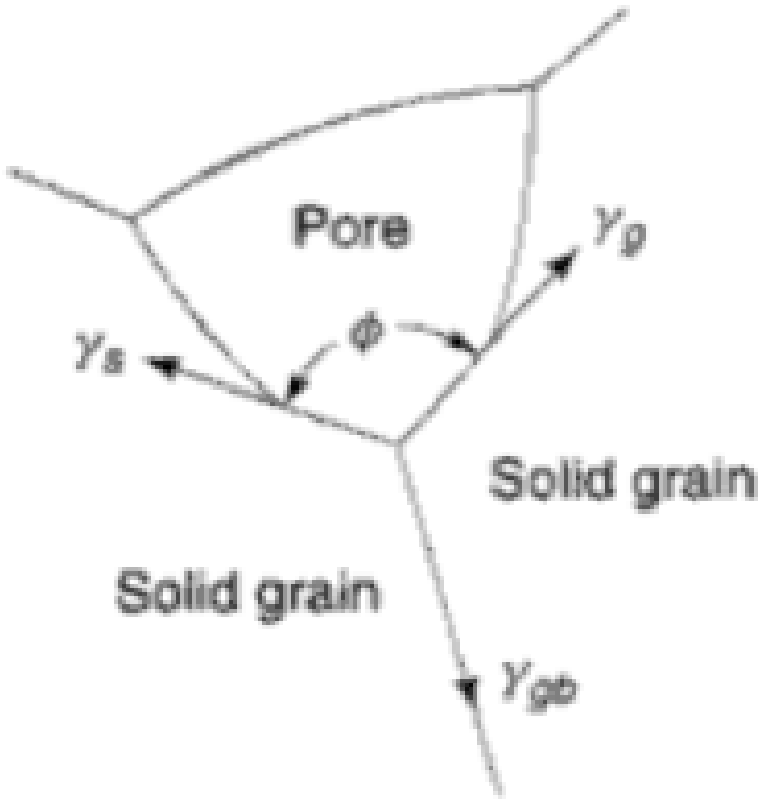


Figure 2.32 Schematic illustration of dihedral angle for solid–pore interaction.

SOLUTION PROCESSING OF POLYMERS

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta G_{mix} = \alpha X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$ For regular solutions

$$\Delta S_{mix} = -R(X_A \ln v_A + X_B \ln v_B) = -k_B(N_A \ln v_A + N_B \ln v_B)$$

$$\Delta H_{mix} = k_B T \chi N_A v_B = RT \chi v_A v_B$$

(χ, is called the Flory–Huggins interaction Parameter)

(χ is zero for ideal mixtures (zero enthalpy of mixing), positive for endothermic mixing, and negative for exothermic mixing.)

Poor solvents have χ close to 0.5

$$\Delta G_{mix} = k_B T[\chi N_A v_B + N_A \ln v_A + N_B \ln v_B]$$

Table 2.5 Some Polymer–Solvent Interaction Parameters at 25°C

Polymer	Solvent	Interaction Parameter χ
cis-Polyisoprene	Toluene ($V_1 = 106$)[a]	0.391
	Benzene ($V_1 = 89.0$)	0.437
Polyisobutylene	Toluene	0.557
	Cyclohexane ($V_1 = 108$)	0.436
Butadiene-styrene	Benzene	0.442
71.5:28.5	Cyclohexane	0.489
Butadiene-acrylonitrile		
82:18	Benzene	0.390
70:30	Benzene	0.486
61:39	Benzene	0.564

[a]Note that V_1 is in cubic centimeters per mole.

Source: F. Rodriguez, *Principles of Polymer Systems*, 2nd ed. Copyright © 1982 by McGraw-Hill Book Company.

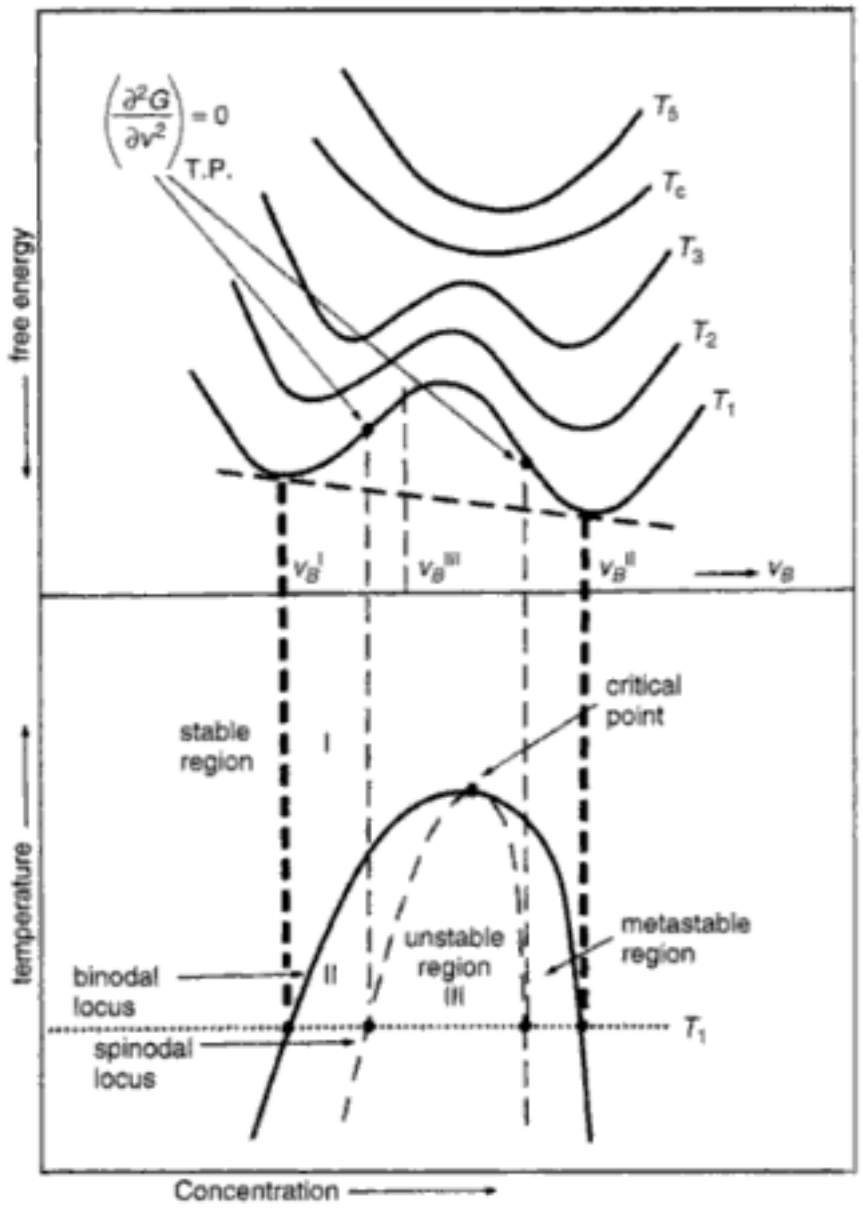


Figure 2.33 Polymer–solvent phase diagram showing binodal, spinodal, and miscibility gap. Reprinted, by permission, from J. M. G. Cowie, *Polymers: Chemistry & Physics of Modern Materials*, 2nd ed., P. 167. Copyright © 1991 by Chapman & Hall.

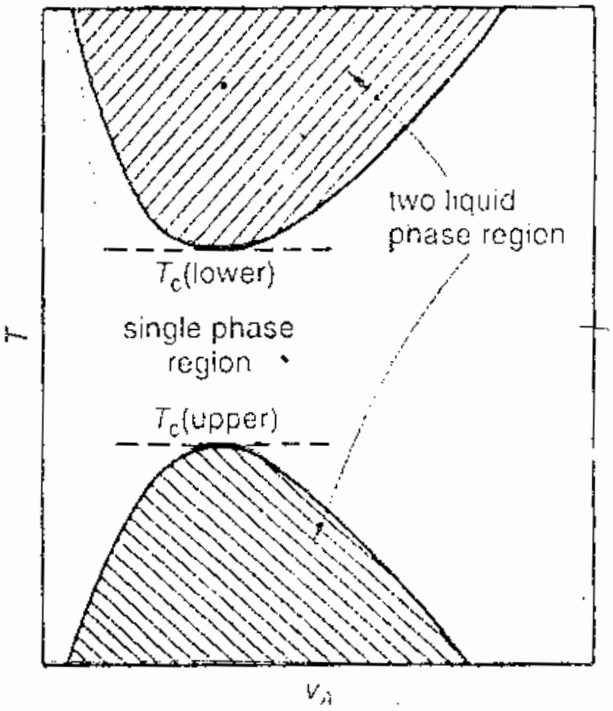


Figure 2.34 Schematic diagram of two phase regions resulting in UCST (*bottom*) and LCST (*top*). Reprinted, by permission, from J. M. G. Cowie, *Polymers: Chemistry & Physics of Modern Materials*, 2nd ed., p. 175: Copyright © 1991 by Chapman & Hall.

Cohesive Energy Density

Solubility parameter, δ

δ^2, called the cohesive energy density

$$\Delta H_{mix} = (\delta_A - \delta_B)^2 v_A v_B$$

$\delta_A - \delta_B$ is less than 3.5 to 4.0 → good solubility

Table 2.6 Typical Values of the Solubility Parameter for Some Common Polymers and Solvents

Solvent	$\delta_A[(J/cm^3)^{1/2}]$	Polymer	$\delta_B[(J/cm^3)^{1/2}]$
n-Hexane	14.8	Polytetrafluoroethylene	12.7
Carbon tetrachloride	17.6	Poly(dimethyl siloxane)	14.9
Toluene	18.3	Polyethylene	16.2
2-Butanone	18.5	Polypropylene	16.6
Benzene	18.7	Polybutadiene	17.6
Cyclohexanone	19.0	Polystyrene	17.6
Styrene	19.0	Poly(methyl methacrylate)	18.6
Chlorobenzene	19.4	Poly(vinyl chloride)	19.4
Acetone	19.9	Poly(vinyl acetate)	21.7
Tetrahydrofuran	20.3	Poly(ethylene terephthalate)	21.9
Methanol	29.7	66-Nylon	27.8
Water	47.9	Polyacrylonitrile	31.5

Source: F. W. Billmeyer, *Textbook of Polymer Science*, 3rd ed. Copyright © 1984 by John Wiley & Sons, Inc.

$$\delta_B = \frac{\rho \sum E}{M_0}$$

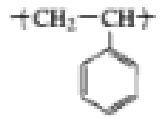
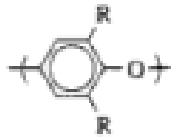
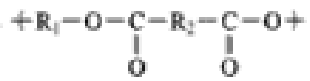
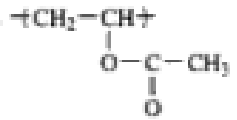
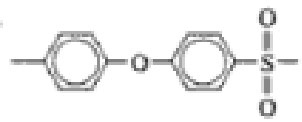
molar-attraction constants, E

Table 2.7 Molar Attraction Constants

Group	$E[(J\text{-}cm^3)^{1/2}/\ mol]$	Group	$E[(J\text{-}cm^3)^{1/2}/\ mol]$
$-CH_3$	303	NH_2	463
$-CH_2-$	269	$-NH-$	368
$>CH-$	176	$-N-$	125
$>C<$	65	$C\equiv N$	725
$CH_2=$	259	NCO	733
$-CH=$	249	$-S-$	429
$>C=$	173	Cl_2	701
$-CH=$ aromatic	239	Cl primary	419
$>C=$ aromatic	200	Cl secondary	425
$-O-$ ether, acetal	235	Cl aromatic	329
$-O-$ epoxide	360	F	84
$-COO-$	668	Conjugation	47
$>C=O$	538	cis	−14
$-CHO$	599	trans	−28
$(CO)_2O$	1159	Six-membered ring	−48
$-OH$	462	ortho	−19
OH aromatic	350	meta	−13
—H acidic dimer	−103	para	−82

Source: F. W. Billmeyer, *Textbook of Polymer Science*, 3rd ed. Copyright © 1984 by John Wiley & Sons, Inc.

Table 2.8 Complementary Groups Found in Miscible Polymer Blends

Group 1	Group 2
1. 	
2. 	
3. 	
4. 	
5. 	
6. 	
7. 	
8. 	

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