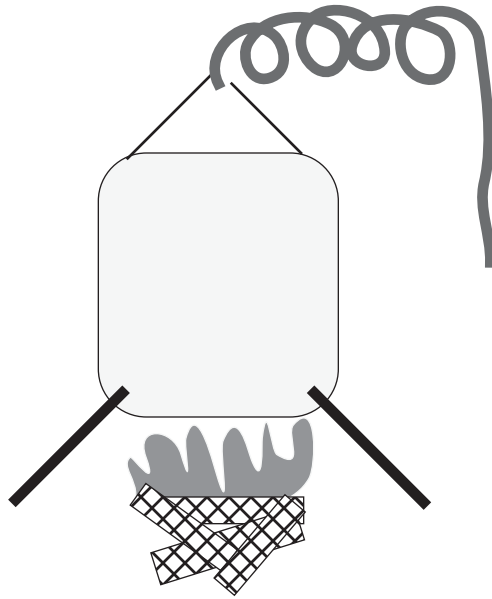
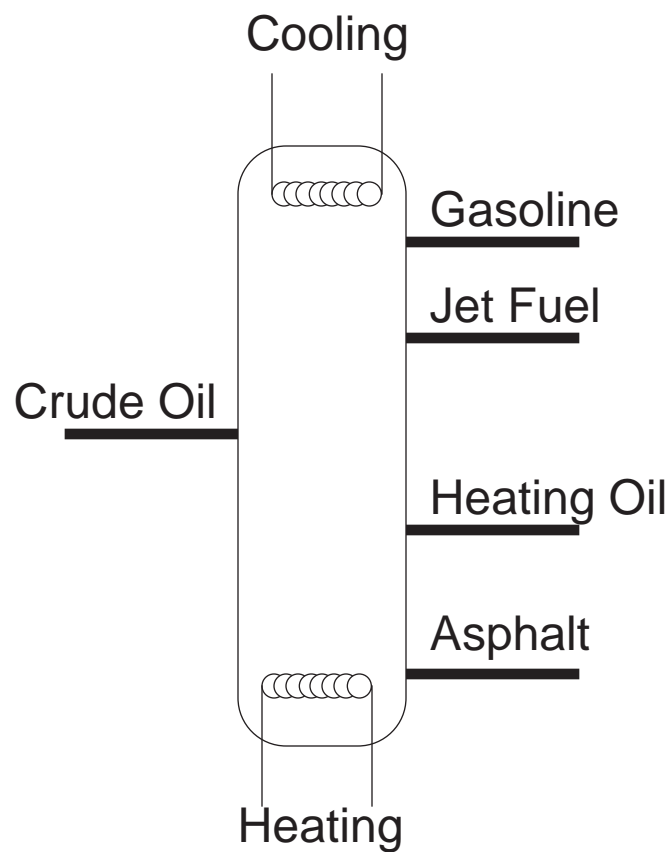


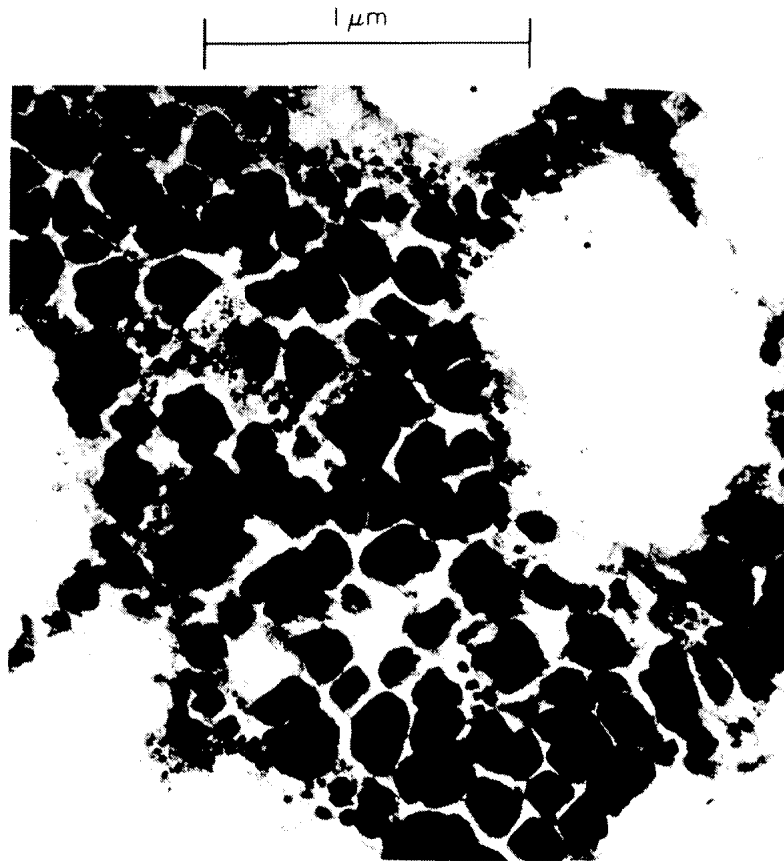
Moonshiners



Oil Producers



Makers of high-strength alloys



How do you calculate phase equilibria?

What does phase equilibrium mean?

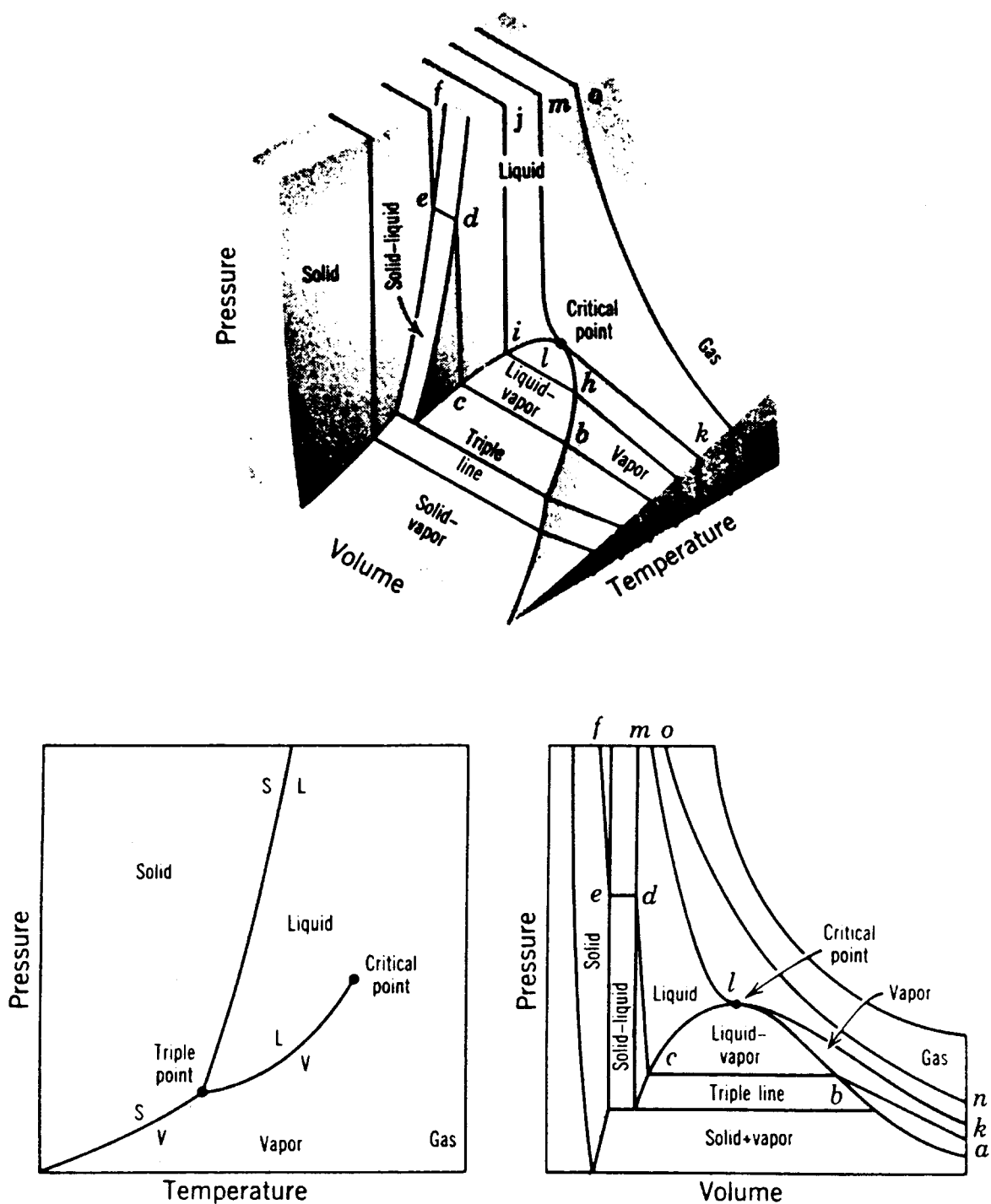


FIGURE 3.11 Pressure-volume-temperature surface for a substance that contracts on freezing.

PHASE EQUILIBRIA IN A ONE-COMPONENT SYSTEM

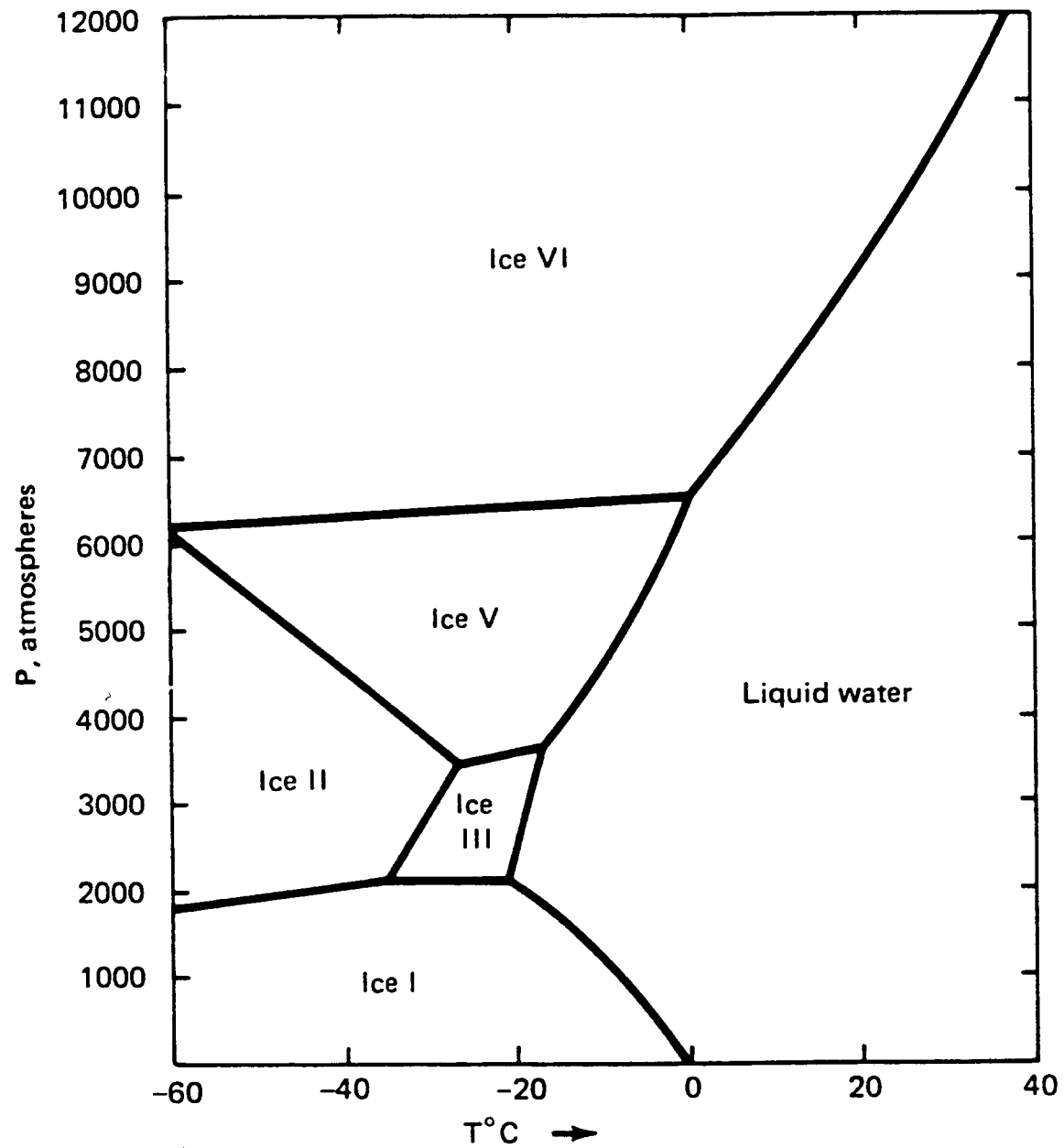
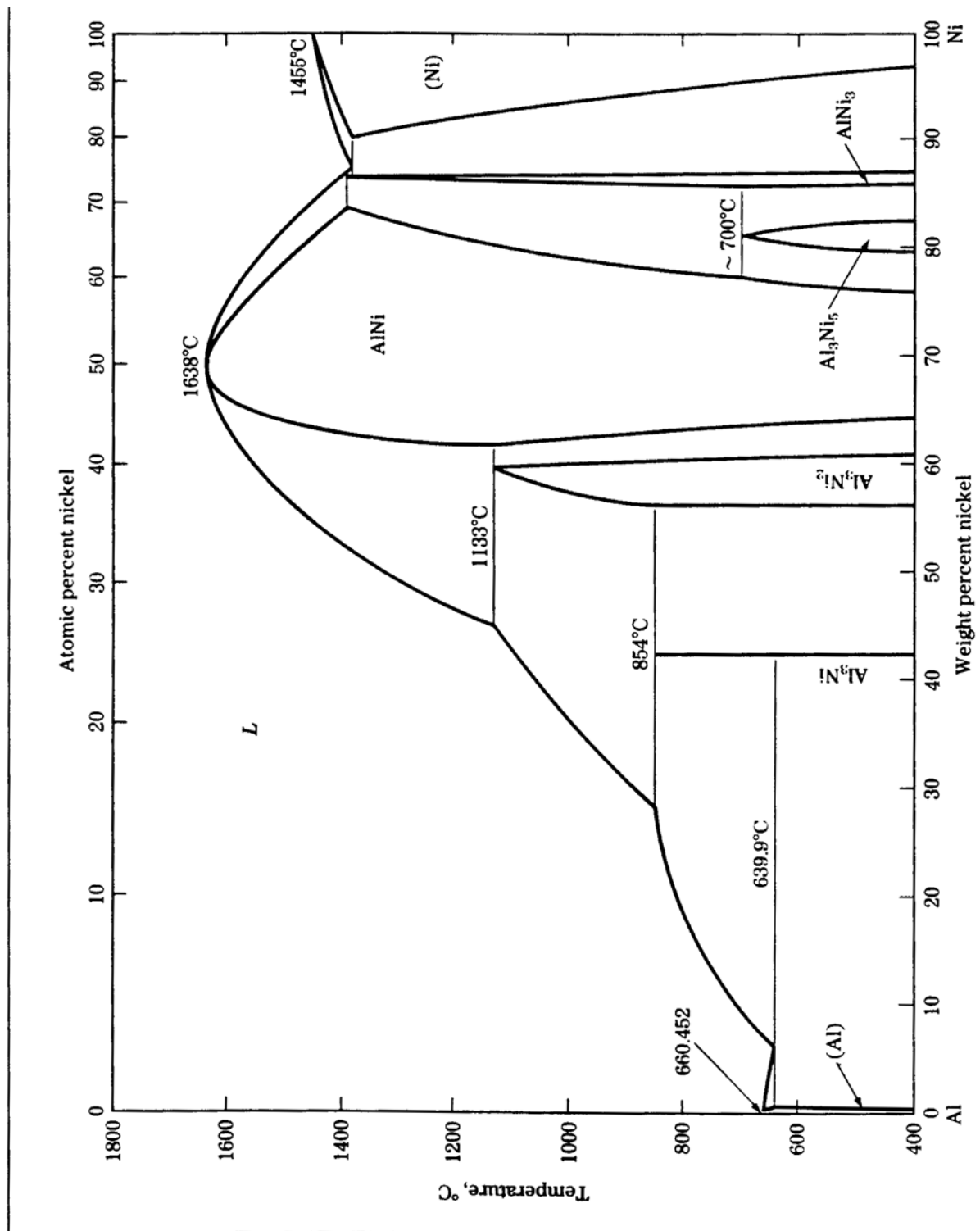


FIGURE 8.33 Aluminum-nickel phase diagram. (After Binary Phase Diagrams, ASM Int., 1986, p. 142).



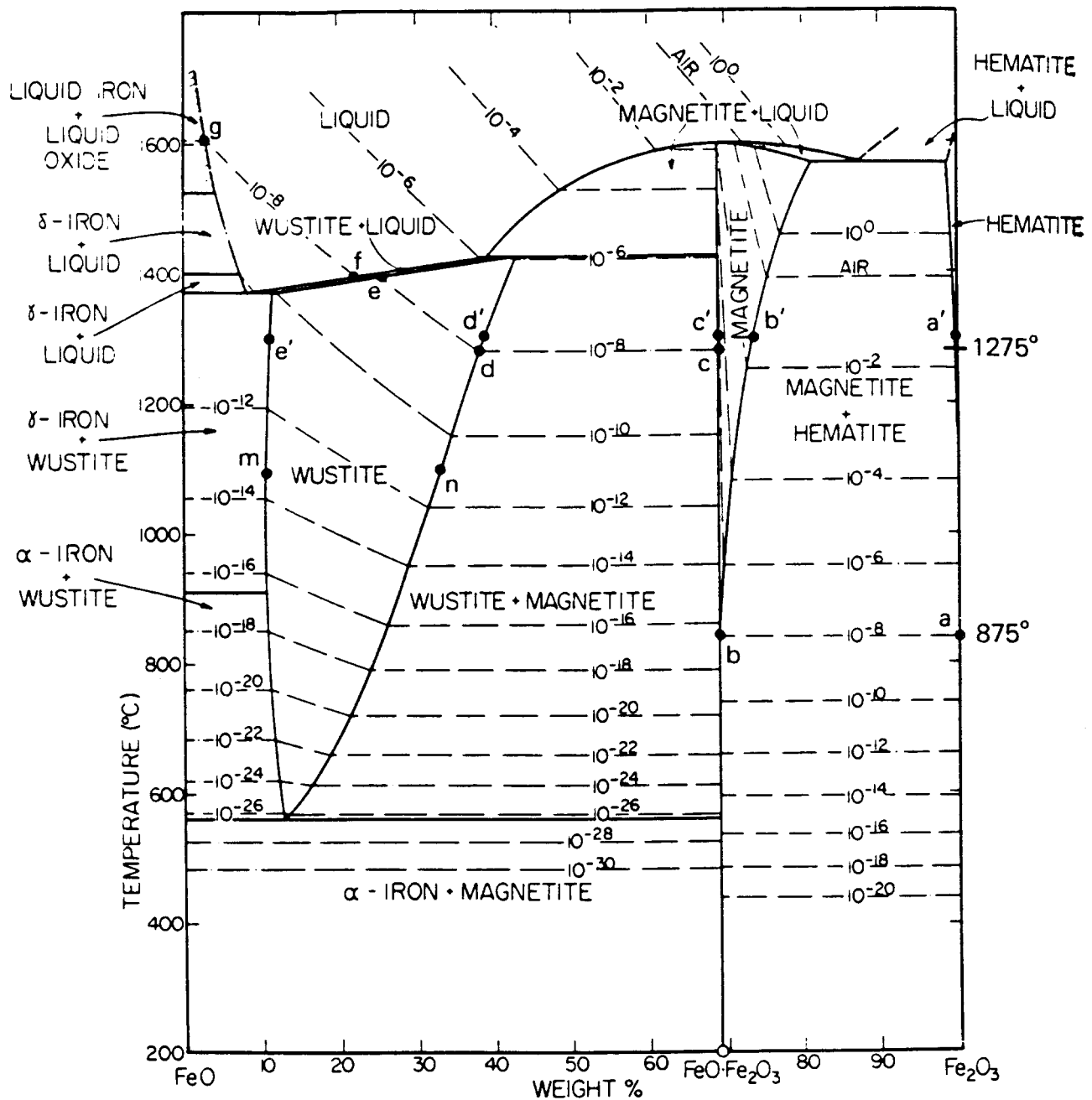


Fig. 13.27. The phase diagram of the system FeO-Fe₂O₃ showing the positions of the oxygen isobars. (From A. Muan and E. F. Osborn, "Phase Equilibria among Oxides in Steelmaking," Addison-Wesley Publishing Co., Reading, Mass., 1965.)

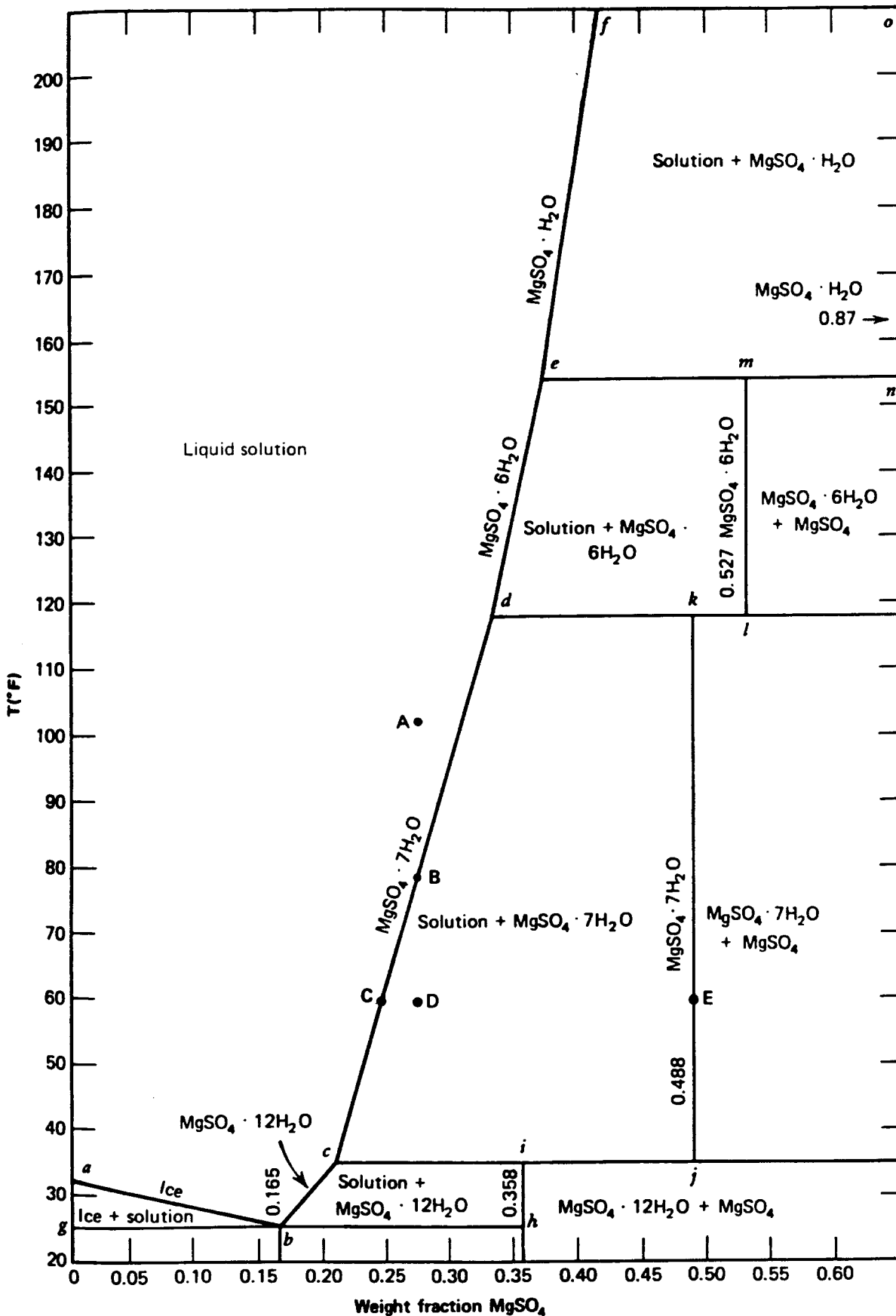


FIGURE 6.5-1

Phase diagram for $\text{MgSO}_4\text{-H}_2\text{O}$. (Adapted from R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook*, 6th Edition, p. 19-26. Copyright ©

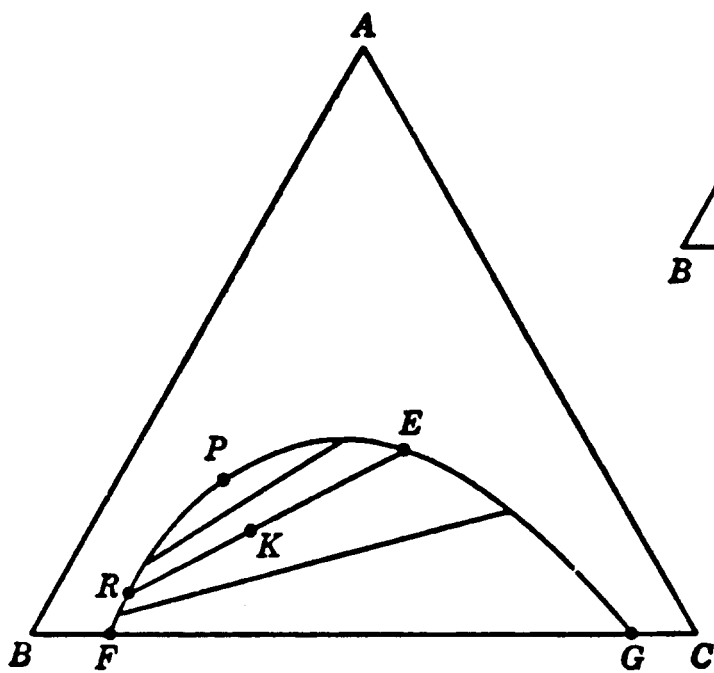


FIG. 32. Type 1 system

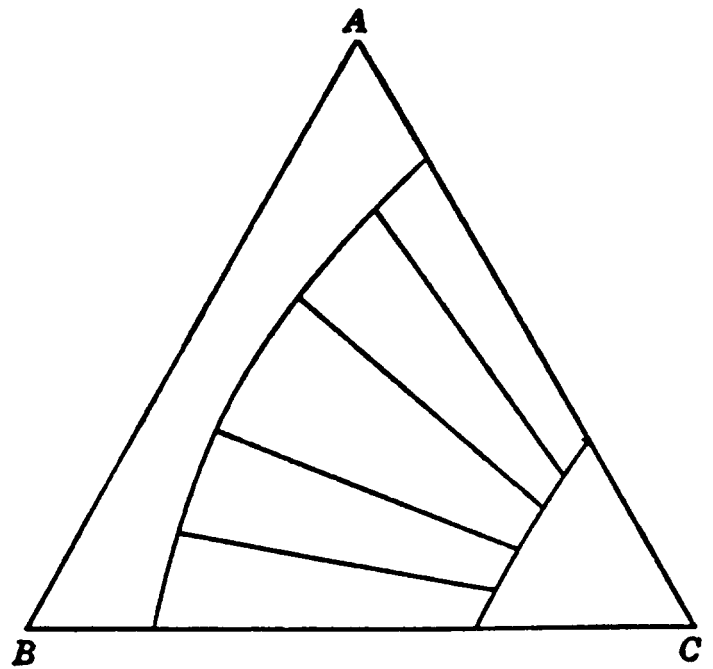


FIG. 34. Type 2 system

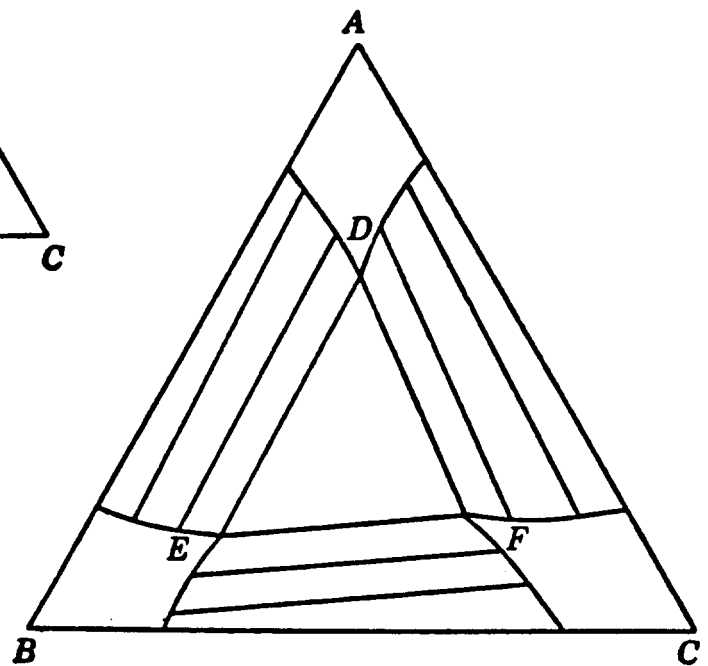


FIG. 35. Type 3 system

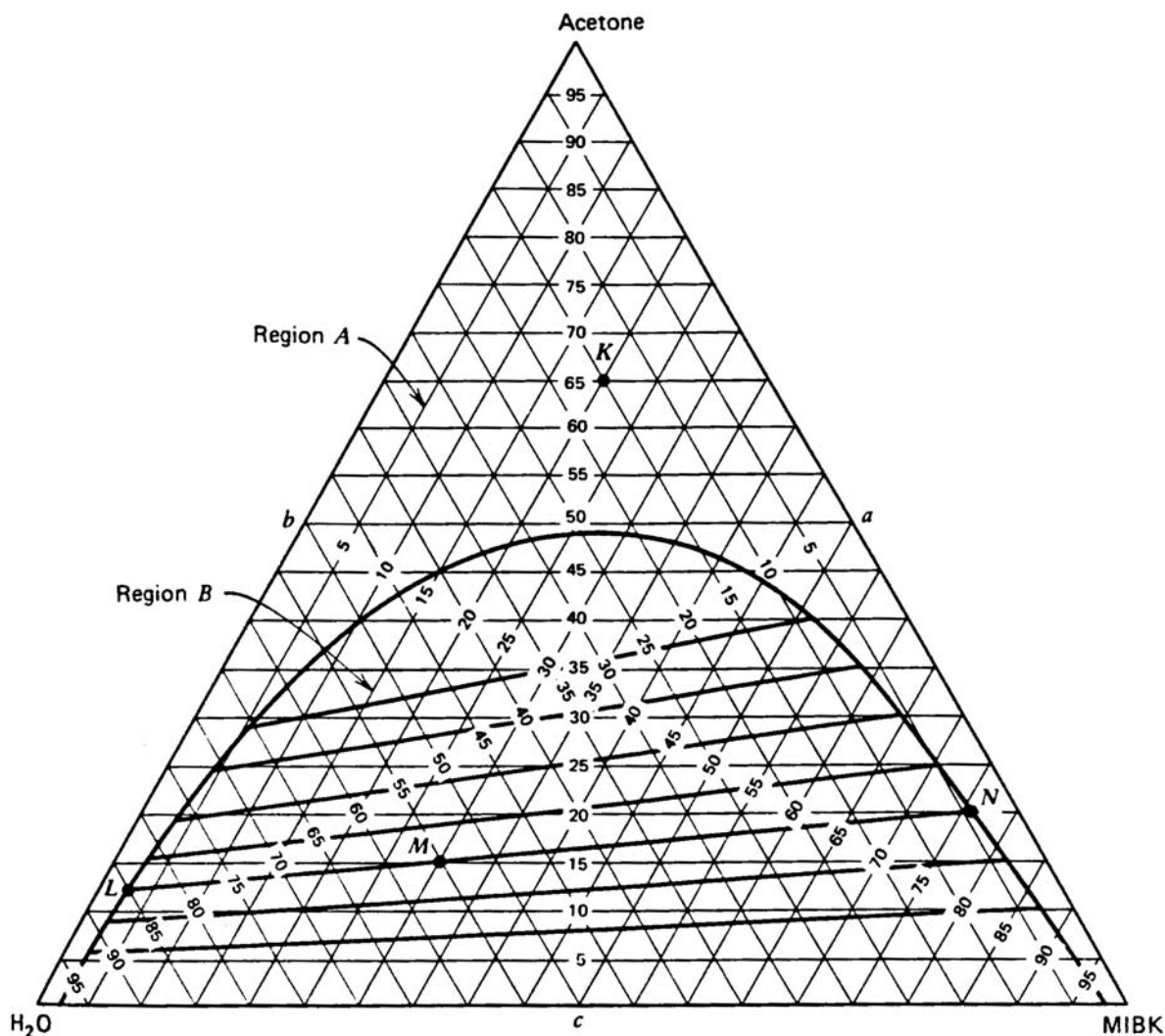
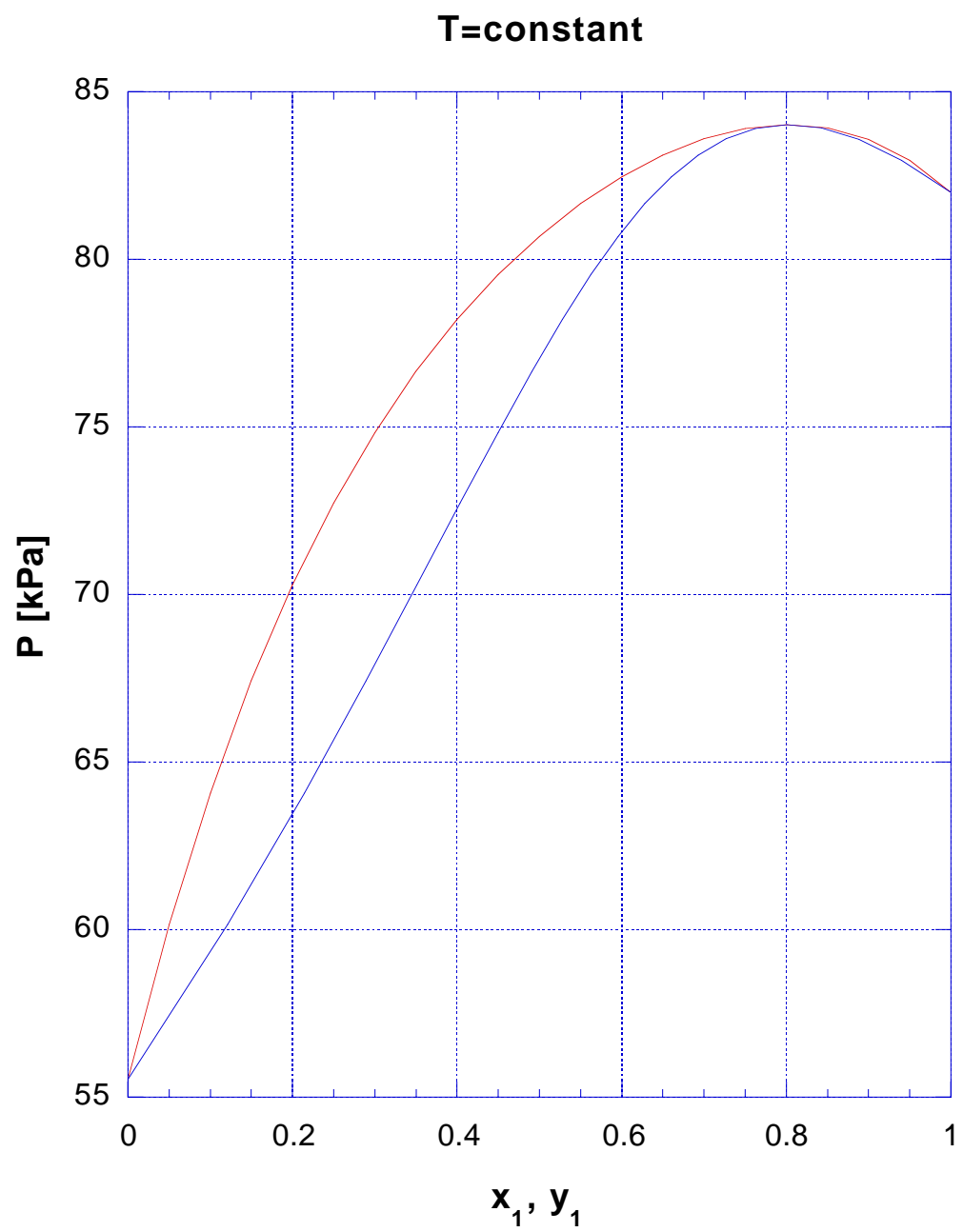
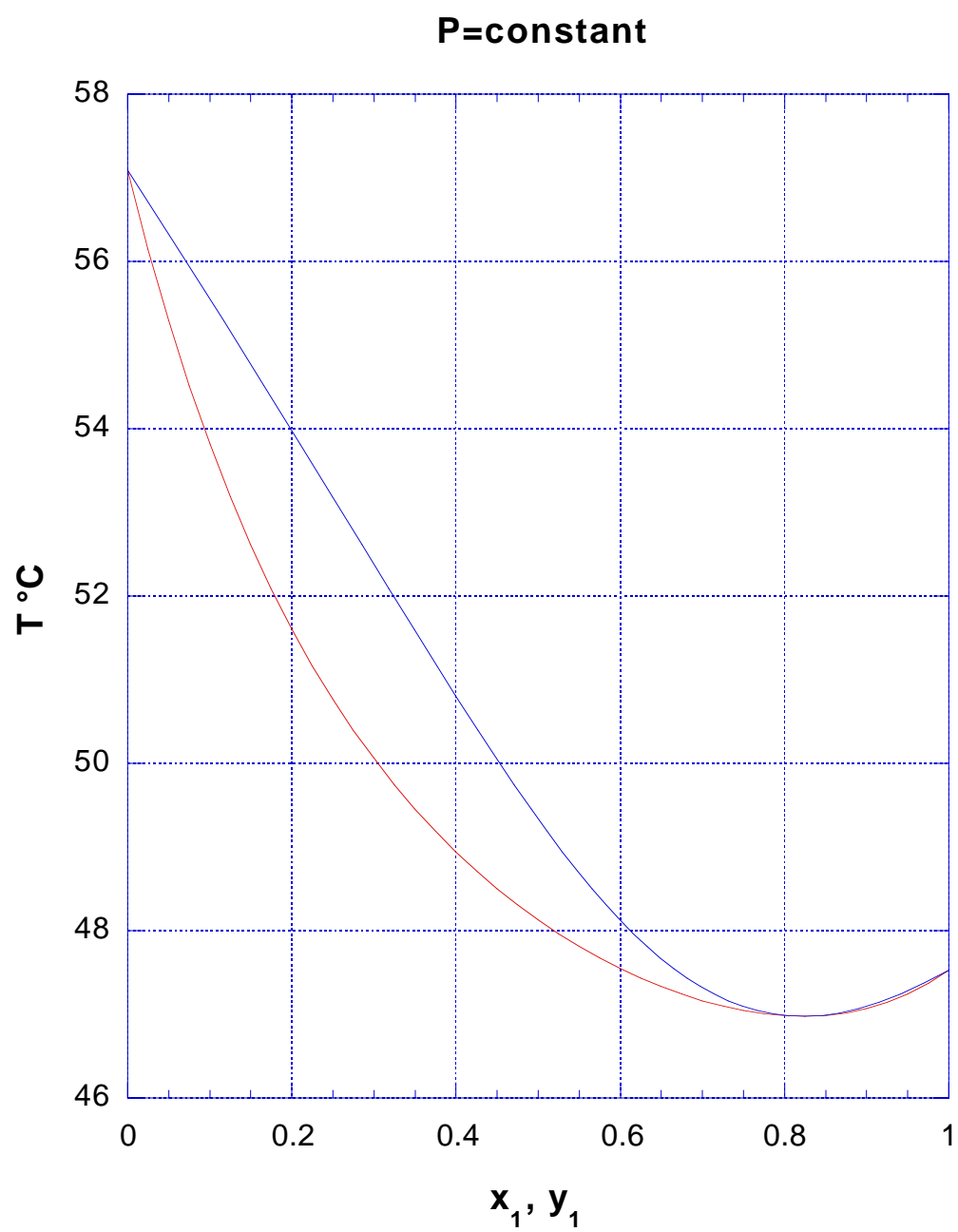


FIGURE 6.6-1

Triangular phase diagram for water-acetone-methyl isobutyl ketone at 25°C.
(From D. F. Othmer, R. E. White, and E. Trueger, *Ind. Eng. Chem.* 33, 1240, 1941.)
(Composition in wt%).





Gibbs' Phase Rule

The **P**olice **F**orce equals the **C**ops plus **2** secretaries

$$P + F = C + 2$$

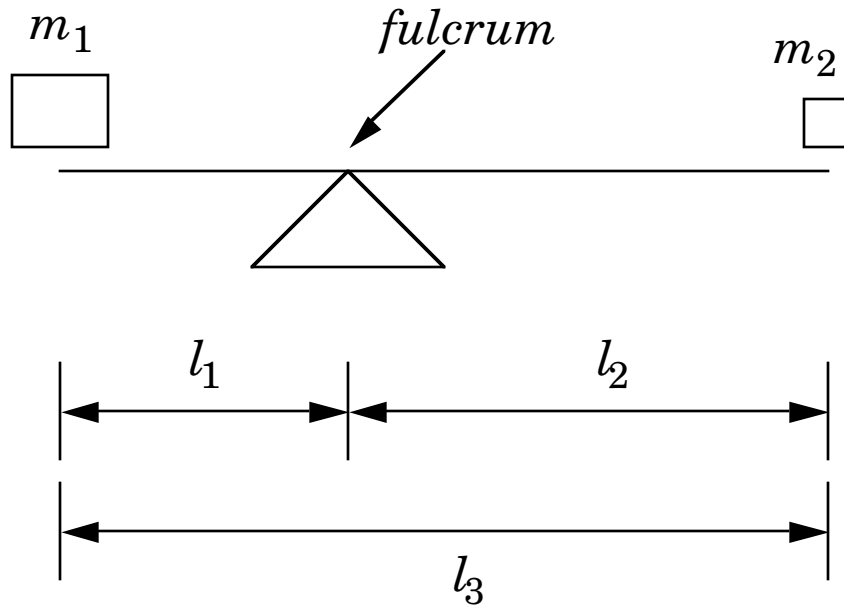
$$DF = 2 + c - \Pi$$

A *Degree of Freedom* is a coordinate or variable.

A *Component* is a chemical species, *e.g.* Al_2O_3 .

A *Phase* is a physical entity with a uniform composition, temperature, pressure and specific volume. In a given container, you can have multiple solid phases and multiple liquid phases, but only one vapor or gas phase.

The Lever Rule



If

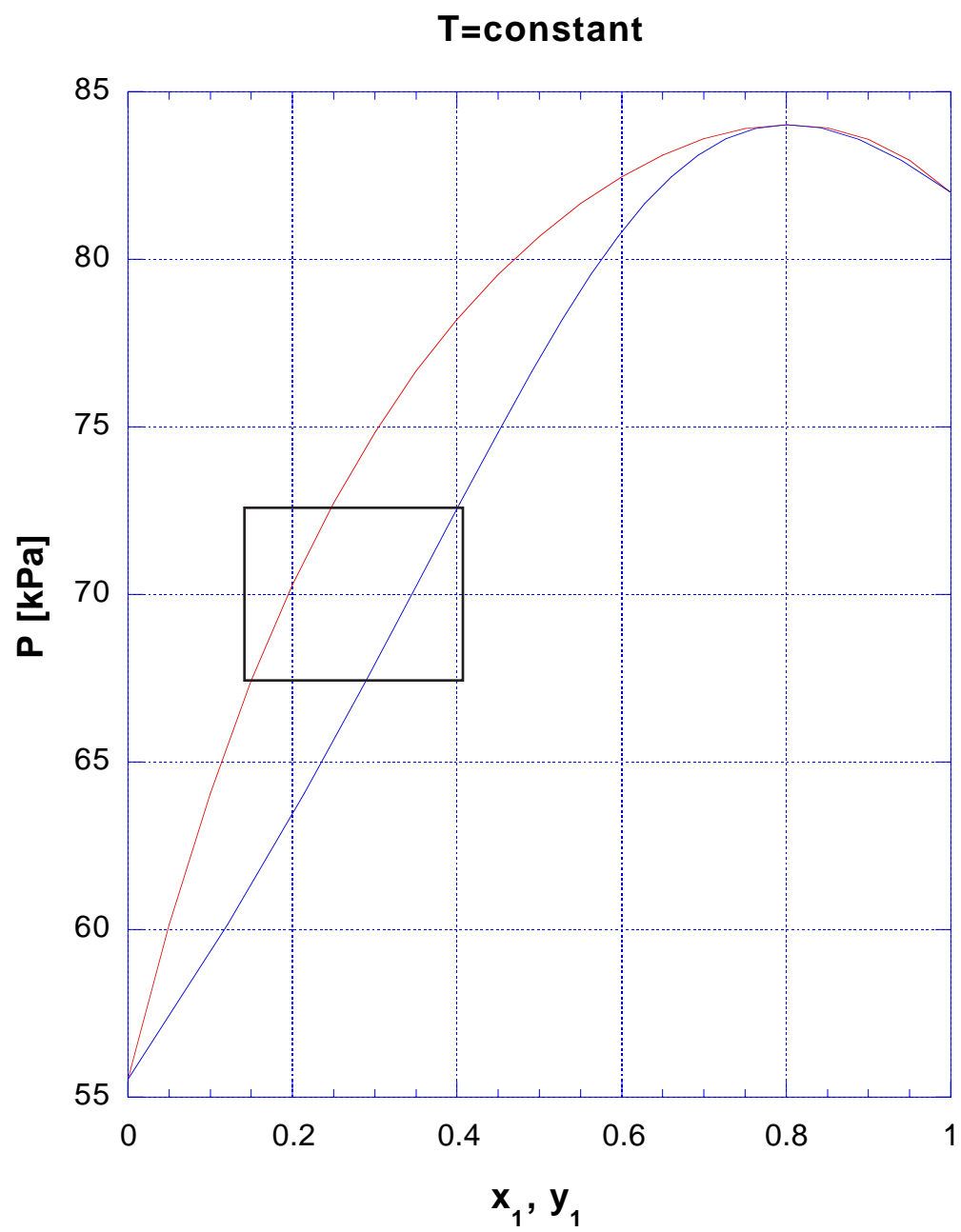
$$m_3 = m_1 + m_2$$

Then

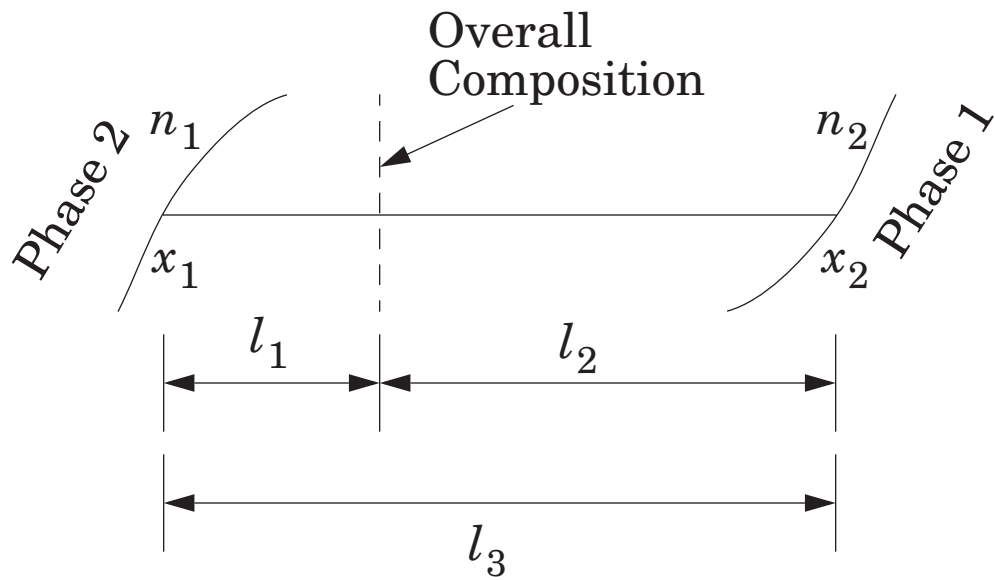
$$m_1 l_1 = m_2 l_2$$

$$\frac{m_1}{m_3} = \frac{l_2}{l_3}$$

$$\frac{m_2}{m_3} = \frac{l_1}{l_3}$$



The Lever Rule for Phase Diagrams



If

$$n_3 = n_1 + n_2$$

Then

$$n_1 l_1 = n_2 l_2$$

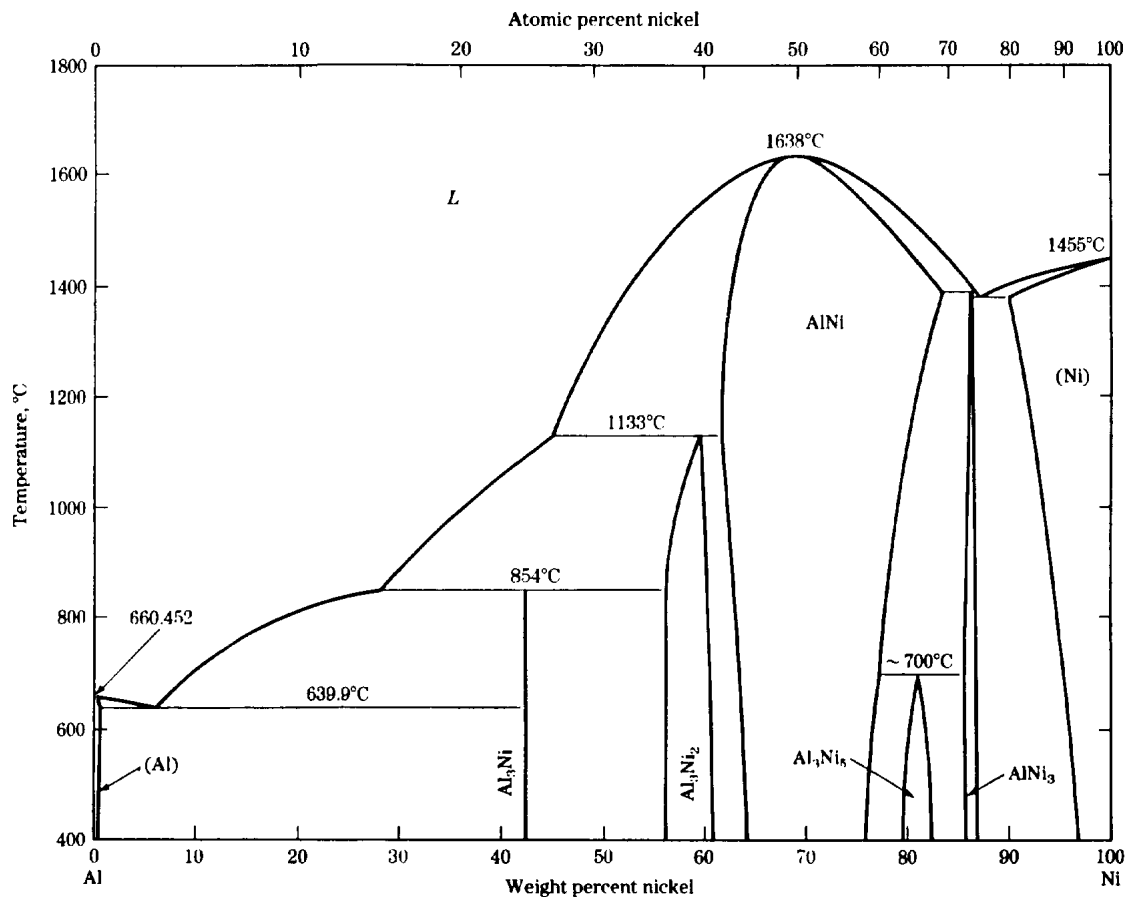
$$\frac{n_1}{n_3} = \frac{l_2}{l_3}$$

$$\frac{n_2}{n_3} = \frac{l_1}{l_3}$$

Example

We have an equilibrium mixture of aluminum and nickel at 1000°C.

50% of the overall mixture is nickel. Give the compositions and relative amounts of all phases present.



If we don't have a phase diagram, or if we wish to automate the calculation procedure, what do we do?

1-Component Vapor-Liquid Equilibrium (VLE)

From Thermodynamics (p 181 in S &V N) comes the *Clapeyron* equation:

$$\frac{dp^*}{dT} = \frac{\Delta\hat{H}_v}{T(\hat{V}_g - \hat{V}_l)}$$

where p^* is the vapor pressure.

If $\hat{V}_g \gg \hat{V}_l$, and the vapor is ideal, then:

$$\frac{d(\ln p^*)}{d(1/T)} = -\frac{\Delta\hat{H}_v}{R}$$

If in addition, $\Delta\hat{H}_v$ is constant, we can integrate to

$$\ln p^* = -\frac{\Delta\hat{H}_v}{RT} + B$$

which is the *Clausius-Clapeyron* equation.

Empirical equations are also used. The simplest with reasonable accuracy is the *Antoine* equation:

$$\log_{10} p^* = A - \frac{B}{T + C}$$

where A , B , and C are constants from a table (*e.g.*, Table B.4 on p. 640 in *Felder*). What are A , B , and C if the substance obeys the Clausius-Clapeyron equation?

Charts and Tables are also available (*e.g.*, Figure 6.1-4 on p. 247, and Tables B-3 through B-6 in Appendix B of *Felder*).

2-Component VLE

1-Condensable component, *e.g.*, ethanol-argon
Assume Ideal Gas Behavior and that species i is the condensable one, then at saturation (*e.g.*, two-phases present):

$$p_i = y_i P = p_i^*(T)$$

If the temperature is high enough (or pressure low enough) that only one phase is present then:

$$p_i = y_i P < p_i^*(T)$$

At what temperature will condensation begin?

$$p_i = y_i P = p_i^*(T_{dp})$$

T_{dp} is the *dew-point* temperature. The difference between T and T_{dp} is the *degree(s) of superheat*.

Example: You are standing in the shower with the air and water temperature at 35°C. What mole-fraction of the air that you are breathing is water?

Example

	A	B	C
	8.10765	1750.286	235
T	35		
log10p	1.62510926		
p*	42.1802607		
y _{H2O}	0.05550034		

It is far too simple to use mole fraction when talking to other people so we have the following definitions (saturation is any gas-vapor system, humidity is specifically air-water):

Relative Saturation or Relative Humidity

$$s_r \text{ or } h_r = \frac{p_i}{p_i^*(T)} \times 100\%$$

Molal Saturation or Molal Humidity

$$s_m \text{ or } h_m = \frac{p_i}{P - p_i} = \frac{\text{moles of vapor}}{\text{moles of vapor-free (dry) gas}}$$

Absolute Saturation or Absolute Humidity

$$s_a \text{ or } h_a = \frac{p_i M_i}{(P - p_i) M_{\text{dry}}} = \frac{\text{mass of vapor}}{\text{mass of dry gas}}$$

Percentage Saturation or Percentage Humidity

$$s_p \text{ or } h_p = 100 \frac{s_m}{s_m^*} = 100 \frac{p_i / (P - p_i)}{p_i^* / (P - p_i^*)}$$

Example: You set out a cold (root)brew on a day when the temperature is 86°F and the relative humidity is 30%. At what temperature is the brew when water quits condensing on the can? (squid question: what are the degrees of superheat?)

T °F	86
T°C	30
log10psat	1.50279717
psat	31.8271074
yH2Osat	0.04187777
yH2O	0.01256333
pdp	9.54813222
log10pdp	0.97991842
Tdp°C	10.5600329
Tdp°F	51.0080592

What about a gas dissolved in a liquid? For dilute solutions, *Henry's Law* holds (A dilute solution is one for which Henry's law holds).

$$p_A \equiv y_A P = x_A H_A(T)$$

In words, the fraction of A dissolved in the liquid phase is directly proportional to the partial pressure of A in the vapor phase. The proportionality constant (which can change with temperature) is the *Henry's Law Constant*. (See Example 6.4-2 part 1 in *Felder*)

Multicomponent Systems

If the vapor phase is an ideal-gas mixture and the liquid phase is an ideal solution then *Raoult's* Law holds.

$$p_A \equiv y_A P = x_A p_A^*(T)$$

or in terms of species i ,

$$y_i P = x_i p_i^*(T) \quad (i = 1, 2, 3, \dots, N)$$

In words, the partial pressure of a component is equal to the liquid mole fraction of the component times its vapor pressure.

(If the vapor phase is not an ideal-gas mixture or the liquid phase is not an ideal solution then we are led to the realms of activity coefficients, fugacities and Poynting factors)

For multicomponent mixtures, five types of calculations are usually performed using Raoult's law:

- BUBL P – Given all x_i 's and T , calculate P at which the first bubble forms, and y_i 's of the bubble.
- BUBL T – Given all x_i 's and P , calculate T at which the first bubble forms, and y_i 's of the bubble.
- DEW P – Given all y_i 's and T , calculate P at which the first droplet condenses, and x_i 's of the droplet.
- DEW T – Given all y_i 's and P , calculate T at which the first droplet condenses, and x_i 's of the droplet.
- FLASH – Given overall composition (z_i 's) and T and P , calculate x_i 's and y_i 's, and relative amounts of vapor, V , and liquid, L .

BUBL P – Given all x_k 's and T , calculate P and y_k 's.

Raoult's Law

$$y_k P = x_k p_k^*(T) \quad (k = 1, 2, 3, \dots, N) \quad (\text{BP 1})$$

can be rearranged as:

$$P = \sum_{k=1}^N x_k p_k^* \quad (\text{BP 2})$$

to calculate P . Then calculate y_k 's from:

$$y_k = \frac{x_k p_k^*}{P} \quad (k = 1, 2, 3, \dots, N) \quad (\text{BP 3})$$

DEW P – Given all y_k 's and T , calculate P and x_k 's.

Given

$$x_k = \frac{y_k P}{p_k^*} \quad (k = 1, 2, 3, \dots, N) \quad (\text{DP 1})$$

and

$$\sum_{k=1}^N x_k = 1 \quad (\text{DP 2})$$

then,

$$1 = P \sum_{k=1}^N \frac{y_k}{p_k^*} \quad (\text{DP 3})$$

and

$$P = \frac{1}{\sum_{k=1}^N \frac{y_k}{p_k^*}} \quad (\text{DP 4})$$

to calculate P . Then calculate x_k 's from (DP1).

BUBL T – Given all x_i 's and P , calculate T and y_i 's.

In general, an iterative solution is required. Pick an arbitrary component, i , then:

$$P = p_i^* \sum_{k=1}^N x_k \frac{p_k^*}{p_i^*} \quad (\text{BT 1})$$

or

$$p_i^* = \frac{P}{\sum_{k=1}^N x_k \alpha_{ki}} \quad (\text{BT 2})$$

where the relative volatility, α_{ki} , is defined as:

$$\alpha_{ki} \equiv \frac{p_k^*}{p_i^*} \quad (\text{BT 3})$$

If the vapor pressures are related by the Antoine equation:

$$\log_{10} p^* = A - \frac{B}{T + C} \quad (\text{BT 4})$$

then we can calculate,

$$\log_{10}\alpha_{ki} = A_k - A_i - \frac{B_k}{T + C_k} + \frac{B_i}{T + C_i} \quad (\text{BT } 5)$$

One can begin the iteration with an initial guess

$$T_0 = \sum_{k=1}^N x_k T_k^{sat}. \quad (\text{BT } 6)$$

This T can be used to evaluate all of the α_{ki} 's in (BT 5) which are then used in (BT 2) to calculate p_i^* , from which a new value of T can be calculated from:

$$T_1 = \frac{B_i}{A_i - \log_{10} p_i^*} - C_i \quad (\text{BT } 7)$$

The iteration is repeated until T doesn't change much from one iteration to the next. (BT 4) is then used to calculate all p_k^* 's, then use (BP 3) to calculate the y_k 's.

Note: For a two-component system, if you are determining the y_i 's as a function of T at constant P , you don't need to iterate. Choose values of T between T_{b1} and T_{b2} , and calculate the y_i 's using (BT 4) and (BP 3).

DEW T – Given all y_i 's and P , calculate T and x_i 's.

In general, an iterative solution very similar to BUBL T is required. Pick an arbitrary component, i , then:

$$P = \frac{p_i^*}{\sum_{k=1}^N y_k \frac{p_i^*}{p_k^*}} \quad (\text{DT 1})$$

or

$$p_i^* = P \sum_{k=1}^N \frac{y_k}{\alpha_{ki}} \quad (\text{DT 2})$$

where the relative volatility, α_{ki} , is defined in (BT 3) and calculated using (BT 5).

The initial guess is:

$$T_0 = \sum_{k=1}^N y_k T_k^{sat} \quad (\text{DT 3})$$

This T can be used to evaluate all of the α_{ki} 's in (BT 5) which are then used in (DT 2) to calculate p^*_i , from which a new value of T can be calculated from:

$$T_1 = \frac{B_i}{A_i - \log_{10} p^*_i} - C_i \quad (\text{DT 4})$$

After convergence we evaluate the x_k 's from:

$$x_k = \frac{y_k P}{p^*_k} \quad (k = 1, 2, 3, \dots, N) \quad (\text{DT 5})$$

FLASH – Given z_i 's and T and P , calculate x_i 's and y_i 's, and relative amounts of vapor, V , and liquid, L .

$$V = \frac{n_{\text{vapor}}}{n_{\text{total}}} \quad (\text{F } 1)$$

and

$$L = \frac{n_{\text{liquid}}}{n_{\text{total}}} \quad (\text{F } 2)$$

so

$$L + V = 1 \quad (\text{F } 3)$$

and

$$z_i = x_i L + y_i V \quad (i = 1, 2, 3, \dots, N) \quad (\text{F } 4)$$

or

$$z_i = x_i(1 - V) + y_i V \quad (i = 1, 2, 3, \dots, N). \quad (\text{F } 5)$$

Let

$$K_i = \frac{p_i^*}{P} \quad (\text{F } 6)$$

K_i is known as a “K-value” or “distribution coefficient”
(actually K_i is defined by

$$K_i = \frac{y_i}{x_i} \quad (\text{F } 7)$$

which for Raoult’s law yields (F 6)).

Substitution into (F 5) yields

$$y_i = \frac{z_i K_i}{1 + V(K_i - 1)} \quad (i = 1, 2, 3, \dots, N) \quad (\text{F } 8)$$

or

$$\sum_{i=1}^N \frac{z_i K_i}{1 + V(K_i - 1)} = 1 \quad (\text{F } 9)$$

which is solved by numerical methods for V . Then find the y_i from (F 8) and the x_i from (F 7).

Example

The binary system benzene/toluene conforms closely to Raoult's law. Vapor pressures for the pure species are given by the following Antoine equations:

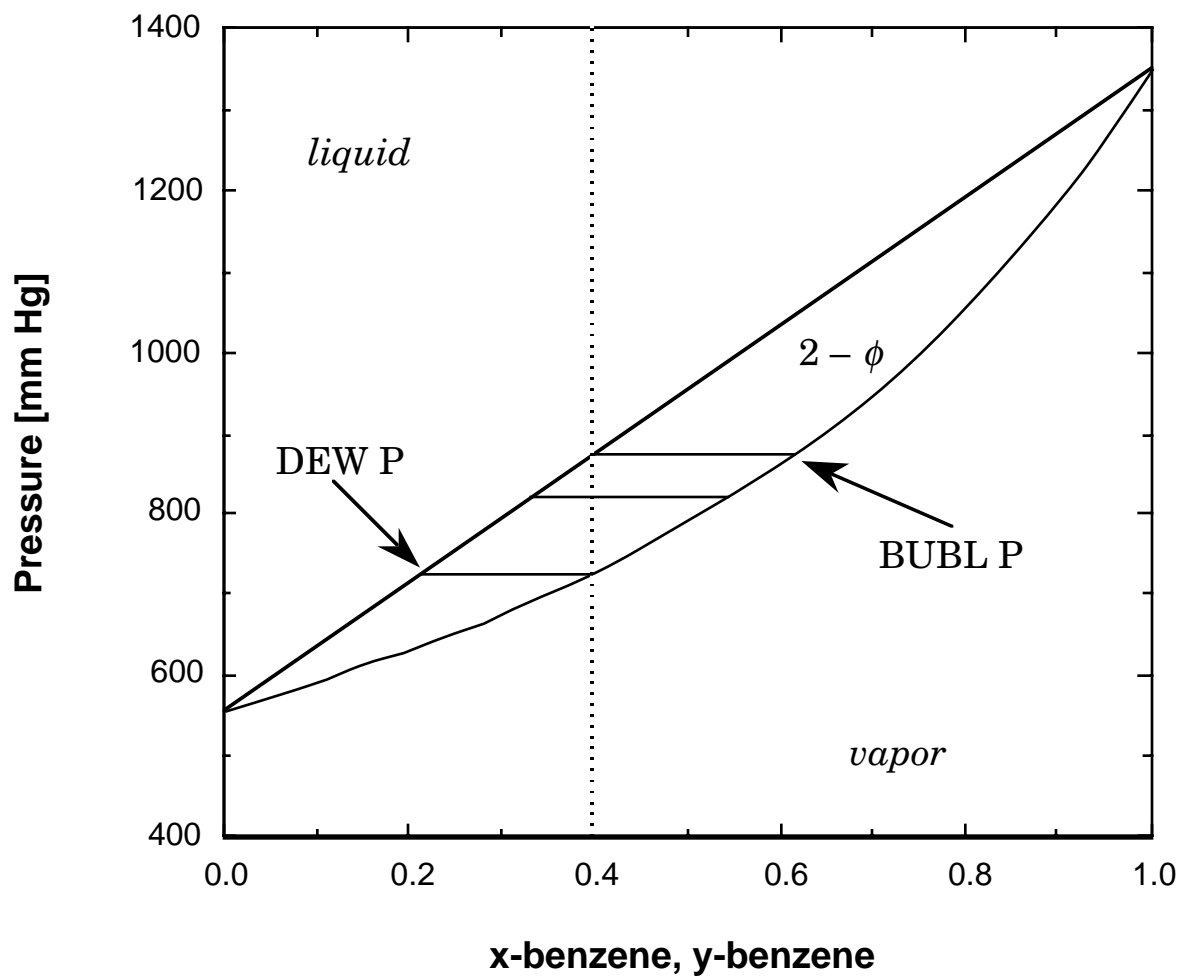
$$\log p_b^*/\text{mm Hg} = 6.89272 - \frac{1203.531}{T/^{\circ}\text{C} + 219.888}$$

$$\log p_t^*/\text{mm Hg} = 6.95805 - \frac{1346.773}{T/^{\circ}\text{C} + 219.693}$$

Prepare a graph showing P vs. x_b and P vs. y_b for a temperature of 100°C .

Prepare a graph showing T vs. x_b and T vs. y_b for a pressure of 1 atm.

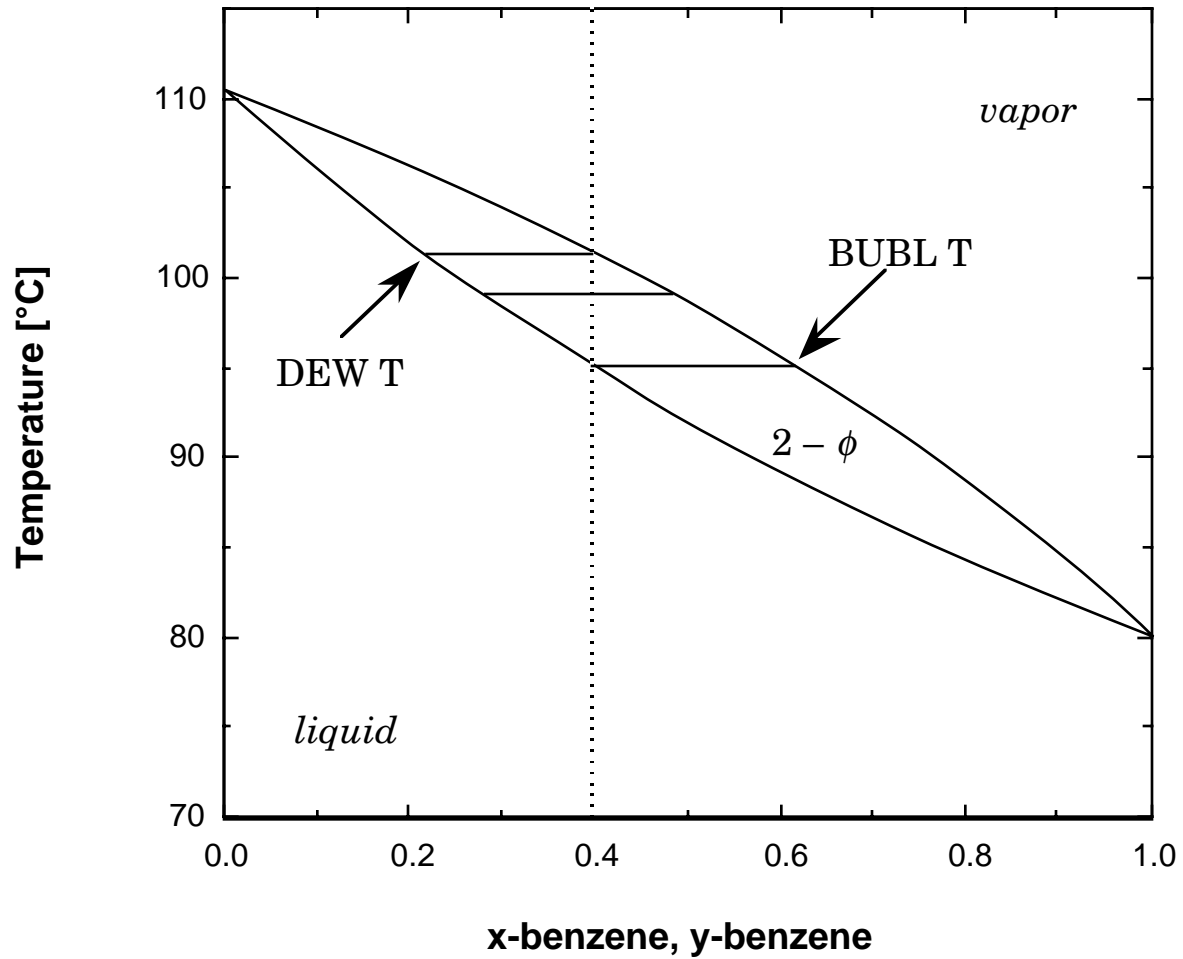
**Pxy Diagram for Benzene/Toluene
at 100°C as given by Raoult's Law**



Calculated Data For Pxy Diagram For benzene/toluene

x_b	P	y_b	P
0.00	556.34	0.00	556.34
0.05	596.03	0.05	573.19
0.10	635.72	0.10	591.10
0.15	675.41	0.15	610.15
0.20	715.16	0.20	630.48
0.25	754.78	0.25	652.21
0.30	794.47	0.30	675.48
0.35	834.16	0.35	700.49
0.40	873.85	0.40	727.41
0.45	913.54	0.45	756.48
0.50	953.23	0.50	787.98
0.55	992.91	0.55	822.21
0.60	1032.60	0.60	859.56
0.65	1072.29	0.65	900.45
0.70	1111.98	0.70	945.44
0.75	1151.67	0.75	995.15
0.80	1191.36	0.80	1050.38
0.85	1231.04	0.85	1112.10
0.90	1270.73	0.90	1181.53
0.95	1310.42	0.95	1260.21
1.00	1350.11	1.00	1350.11

**Txy Diagram for Benzene/Toluene
at 1 atm as given by Raoult's Law**



Calculated Data For Txy Diagram For benzene/toluene

T	x_b	T	y_b	p_b^*	p_t^*
80.10	1.00	80.10	1.00	760.00	292.24
81.63	0.93	81.63	0.97	796.38	307.95
83.15	0.85	83.15	0.94	834.10	324.34
84.68	0.79	84.68	0.90	873.21	341.43
86.21	0.72	86.21	0.87	913.73	359.23
87.73	0.66	87.73	0.83	955.70	377.77
89.26	0.60	89.26	0.79	999.16	397.07
90.78	0.55	90.78	0.75	1044.14	417.15
92.31	0.49	92.31	0.71	1090.67	438.04
93.84	0.44	93.84	0.66	1138.80	459.75
95.36	0.39	95.36	0.61	1188.55	482.31
96.89	0.35	96.89	0.56	1239.96	505.75
98.41	0.30	98.41	0.51	1293.07	530.08
99.94	0.26	99.94	0.46	1347.92	555.33
101.47	0.22	101.47	0.40	1404.54	581.53
102.99	0.18	102.99	0.34	1462.96	608.70
104.52	0.14	104.52	0.28	1523.24	636.87
106.04	0.10	106.04	0.21	1585.40	666.06
107.57	0.07	107.57	0.15	1649.48	696.29
109.10	0.03	109.10	0.07	1715.52	727.60
110.62	0.00	110.62	0.00	1783.55	760.00