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THE DERIVATION OF STABLE UNARY PHASE DIAGRAMS THROUGH THE USE OF DUAL NETWORKS

F. B. KUJAWA, C. A. DUNNING, and H. P. EUGSTER

The Johns Hopkins University, Baltimore, Maryland

ABSTRACT. Unary phase diagrams of stable equilibria can be derived with the aid of Dual networks. For each basic form of these phase diagrams there exists a unique Dual network. In addition, the elements of the two are related by a one-to-one correspondence such that areas correspond to points and line intervals to line segments. Systems with up to 7 phases yield 86 different diagrams, all of which are presented here, together with the corresponding Dual networks. Solutions for 8 and 9 phases are tabulated. The results are helpful for deriving metastable diagrams and diagrams for more than one component.

Equilibrium relationships between phases in heterogeneous systems are the subject of much recent research in geochemistry and geophysics. More and more complicated systems are being investigated to reduce extrapolation from laboratory models to natural phenomena. With the exception of the work by Palatnik and Landau (1964), little effort has been made to extend the generalized geometric solutions offered by Bakhuis Roozeboom (1901, 1904) for unary and binary systems and by Schreinemakers (1911, 1913) for ternary systems. The work at extreme pressures, which is rapidly changing our views of mantle chemistry and physics, has again focused attention on the importance of polymorphic transformations in simple systems. With the number of known high-pressure polymorphs increasing continually, it would be helpful to have a method to derive all possible geometric arrangements of phase boundaries for a system with a given number of components and phases. In this paper, we present such a method for unary phase diagrams of stable equilibria as well as a survey of all solutions for up to seven stable phases. Subsequent papers will deal with extensions and applications of this method to systems of more than one component. They will also treat metastable equilibria.

DEFINITION OF SYMBOLS

C	the number of components, which is the minimum number of chemical formuli necessary to define the composition of all phases present in a chemical system.
ϕ	the number of coexisting phases represented by a particular primary geometric element. A primary[1] geometric element of a phase diagram is the locus of all those points that represent the existence of a particular phase or of an assemblage of coexisting phases.
Φ	the total number of phases present in a chemical system, that is, the total number of phases represented by all the primary geometric elements in a complete phase diagram.
$E\binom{\phi}{\Phi}$	the number of primary geometric elements for a given set of values for Φ and ϕ.
W	the variance or number of degrees of freedom of a particular primary geometric element and of the assemblage of phases represented by that element.
D	the number of geometrically distinct phase diagrams for given values of C and Φ.
D_B	the number of geometrically distinct basic forms of phase diagrams for given values of C and Φ. For the definition of unary basic form, see p. 433.
n	the number of outside points or line segments in a Dual network or the number of unbounded areas in the basic form of a stable unary phase diagram.
d	the number of diagonals in a Dual network or the number of line segments separating unbounded areas in the basic form of a stable unary phase diagram.
s	(as a subscript) stable.

[1] This is to distinguish such elements from conjugate elements of the type L(S) and S(L) as defined by Greig (1955).

A phase diagram consists of a number of primary geometric elements, each of which represents the existence or coexistence of ϕ phases. The relationship between the variance W of an element and ϕ is given by the Gibbs phase rule:

$$W = C + 2 - \phi \geqslant 0 \qquad (1),$$

which must be satisfied for each of the primary geometric elements. Since $\phi \geqslant 1$

$$0 \leqslant W \leqslant C + 1 \qquad (2).$$

Thus a complete phase diagram must have C + 1 dimensions. Also, because $0 \leqslant C + 2 - \phi$,

$$1 \leqslant \phi \leqslant C + 2 \qquad [\text{if } C + 2 \leqslant \Phi] \qquad (3a).$$

But by definition ϕ cannot exceed Φ, thus:

$$1 \leqslant \phi \leqslant \Phi \qquad [\text{if } C + 2 \geqslant \Phi] \qquad (3b).$$

Finally, for a given number of different phases Φ, the number of primary geometric elements $E\binom{\Phi}{\phi}$ is given by the binomial coefficient expression for combinations of Φ phases taken ϕ at a time, or

$$E\binom{\Phi}{\phi} = \frac{\Phi\,!}{\phi\,!\,(\Phi - \phi)\,!} \qquad (4).$$

From the limits of ϕ defined in (3a) and (3b), the total number of primary geometric elements Σ E in a given complete phase diagram is:

$$\Sigma E = \sum_{\phi=1}^{\phi=C+2} E\binom{\Phi}{\phi} \qquad [\text{if } C + 2 \leqslant \Phi] \qquad (5a).$$

$$\Sigma E = \sum_{\phi=1}^{\phi=\Phi} E\binom{\Phi}{\phi} = 2^{\Phi} - 1 \qquad [\text{if } C + 2 \geqslant \Phi] \qquad (5b).$$

For a given number of components C and phases Φ, these Σ E geometric elements can be combined in a number of ways to produce D geometrically different phase diagrams.

Table 1 lists all the values of $E\binom{\Phi}{\phi}$ for $3 \leqslant \Phi \leqslant 12$. The bottom line of the table indicates how far to the right the table is meaningful for a given value of C. For example, all values of $E\binom{\Phi}{\phi}$ to the right of $\phi = 6$ have no meaning in a quaternary system (C = 4) because by (3), ϕ cannot exceed C + 2. Some of the information contained in table 1 and relation (4) has been presented by Korzhinskii (1959), Zharikov (1961), and Palatnik and Landau (1964).

It is obvious toward the bottom of table 1 that the number of elements is rapidly getting out of hand. However, $E\binom{\Phi}{\phi}$ includes both the stable and the metastable primary elements of a phase diagram, and as the number of elements increases, the fraction that are stable decreases rapidly. Thus, even after it has become impractical to depict all the elements, it is often still relatively easy to construct a diagram showing only the stable elements.

TABLE 1

Number of primary geometric elements, $E\binom{\Phi}{\phi}$

No of Phases (Φ)	Number of phases per element (ϕ) 1	2	3	4	5	6	7	8	9	10	11	12	$\sum_{\phi=1}^{\phi=\Phi} E$
3	3	3	1										7
4	4	6	4	1									15
5	5	10	10	5	1								31
6	6	15	20	15	6	1							63
7	7	21	35	35	21	7	1						127
8	8	28	56	70	56	28	8	1					255
9	9	36	84	126	126	84	36	9	1				511
10	10	45	120	210	252	210	120	45	10	1			1023
11	11	55	165	330	462	462	330	165	55	11	1		2047
12	12	66	220	495	792	924	792	495	220	66	12	1	4095
C			1	2	3	4	5	6	7	8	9	10	

Phase diagrams can be rigorously and completely derived from Gibbs free energy diagrams, using what Gibbs (1928) called ξ surfaces. However, this paper will be restricted to the stable equilibria of unary systems, so that such a complete derivation is unnecessary. Instead, we shall employ the following geometrical requirements:

> A unary phase diagram of stable equilibria consists of a pressure-temperature (P-T) plane which is divided into one-phase bivariant *areas* by two-phase univariant *curves* which meet at three-phase invariant *triple points.*
>
> Exactly three curves meet (and terminate) at each triple point in such a way that each of the three angles thus formed is less than 180°.

The first of these requirements follows directly from the phase rule (1) whereas the second can easily be demonstrated with the aid of free energy diagrams (see for instance, Darken and Gurry, 1953, p. 311). Using these requirements,

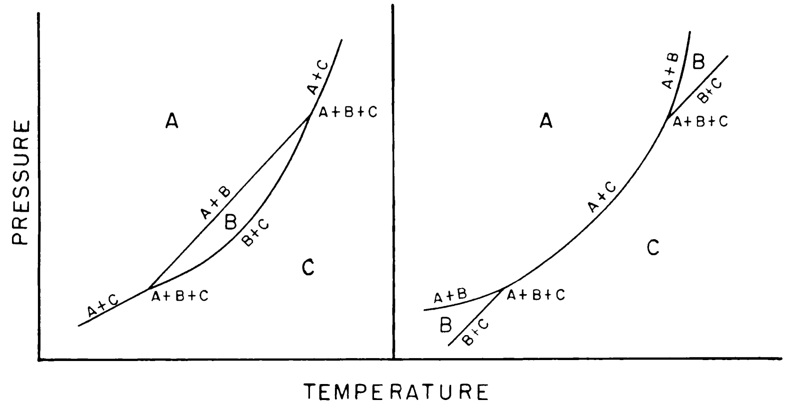


Fig. 1. Examples of unary phase diagrams where some assemblages are represented by more than one primary geometric element.

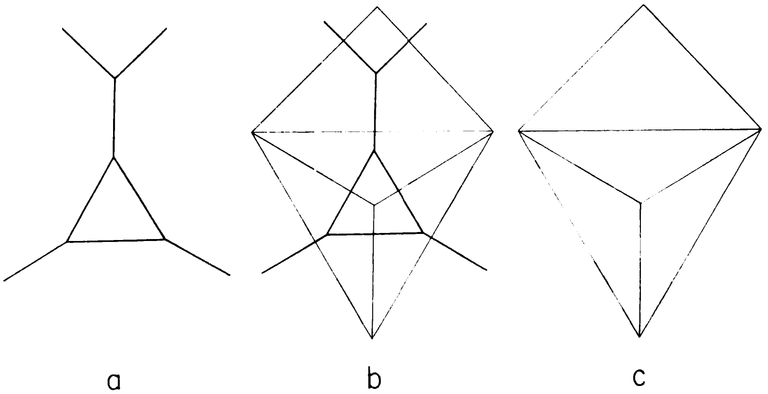


Fig. 2. Comparison of a unary basic form with the corresponding Dual network: (a) unary basic form, (b) superposition, (c) Dual network.

we can construct possible phase diagrams, even for large numbers of phases, but it is often desirable to draw all variations, particularly when little is known about the locations of several of the elements. In this paper, we shall discuss all the possibilities for $\Phi_s \leqslant 7$.

Generally a one–to–one correspondence is assumed to exist between phase assemblages and the primary geometric elements that represent these assemblages. This assumption is valid for all known unary diagrams but is not a necessary requirement. For example, the two diagrams in figure 1 are improbable, but they are nonetheless thermodynamically possible (see also, Bakhuis Roozeboom, 1901, p. 100 and 102). Both have two separate and distinct elements representing the same assemblage A + B + C. In other words, the Gibbs free energies of the phases A, B, and C are equal at two different pairs of P-T values, a highly unlikely event. Such diagrams will therefore be excluded from the subsequent discussion by assuming the one–to–one correspondence mentioned earlier.

An equivalent but geometrically more useful method of making this exclusion is to replace all stable branches of univariant curves with portions of straight lines. These linear portions will be referred to as *line intervals*, and

TABLE 2

Correspondence of geometric elements

ϕ	W	Unary basic form		Dual network
1	2	Area		Point
		a) Bounded area		a) Inside point
		b) Unbounded area		b) Outside point
2	1	Line interval		Line segment $\perp$ Line interval
		a) Line segment	(both ends bounded)	a) Inside line segment
		b) Ray	(one end bounded)	b) Outside line segment
3	0	Triple point		Triangular area

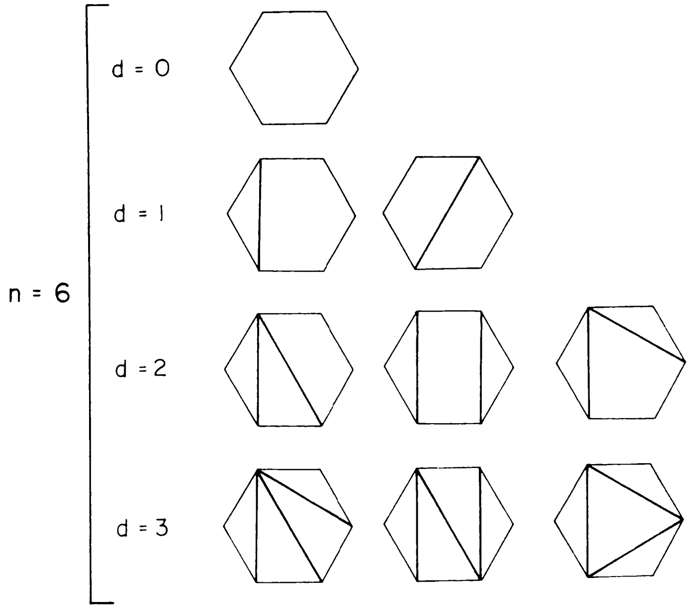


Fig. 3. Ways of inserting d diagonals into a hexagon ($n = 6$) to form frames of Dual networks.

they will include both finite *line segments*, which are bounded by two triple points, and infinite *rays*, which are bounded on only one end.

We shall call these straight-line diagrams *unary basic forms* to distinguish them from actual phase diagrams. In addition, we shall define two properties of unary basic forms to be:

1. Each form lies in a plane that can be extended indefinitely in all directions.
2. In this plane, all orientations of the same geometrical form are equivalent.

Hence, in a unary basic form, all converging line intervals can be extended to form triple points, and all parallel line intervals can be considered to be the same as diverging line intervals.

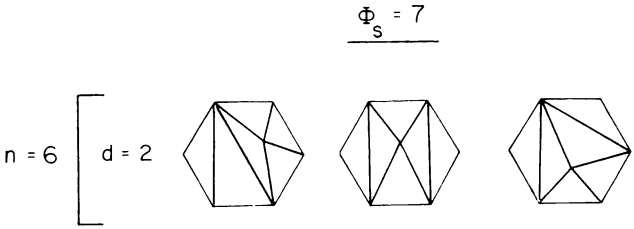


Fig. 4. Ways of inserting one point into the hexagonal frames having two diagonals in order to form Dual networks.

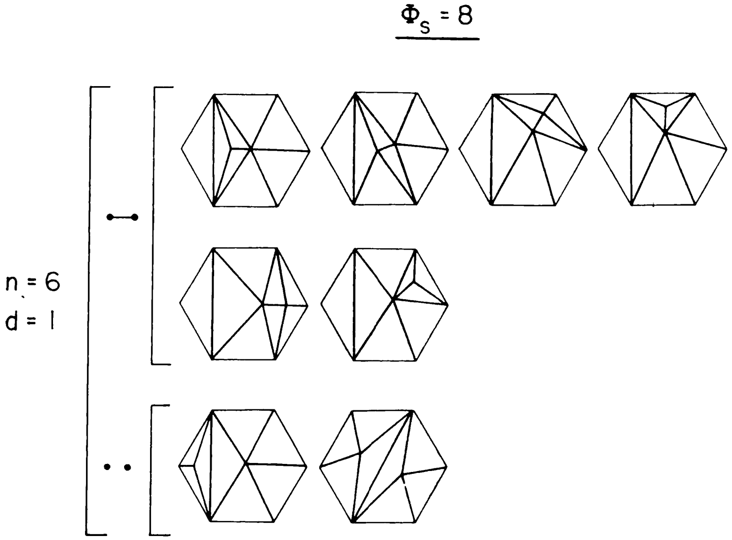


Fig. 5. Ways of inserting two points into the hexagonal frames having one diagonal in order to form Dual networks.

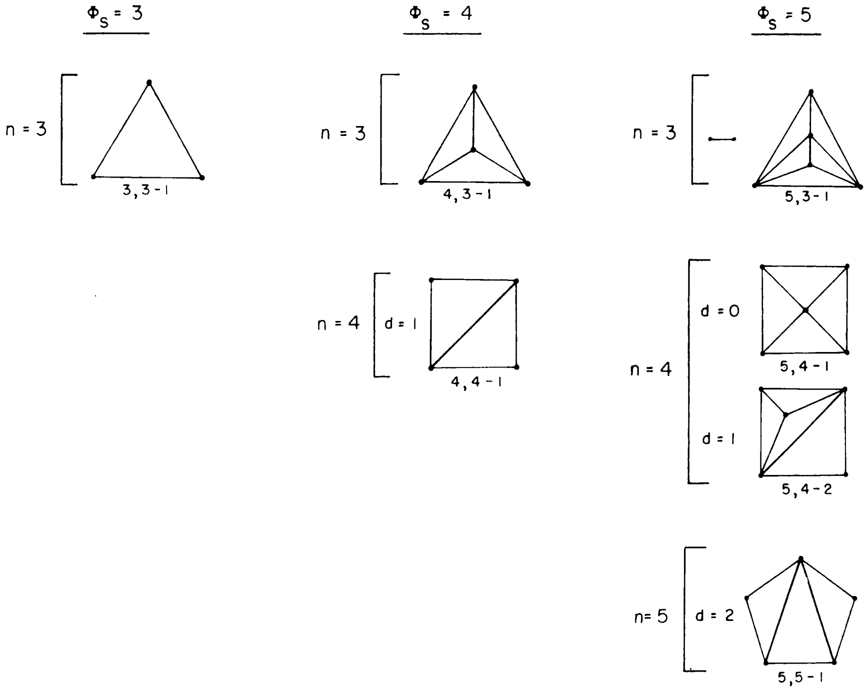


Fig. 6. Dual networks for 3, 4, and 5 stable phases, where n is the number of outside points and d is the number of diagonals. The diagrams are numbered in the order of their derivation according to the scheme: Φ_s, n – arbitrary number.

The problem of deriving and enumerating all possible unary basic forms for a given number of stable phases (Φ_s) can now be stated as follows:

> How many different ways are there of dividing a completely unbounded plane into Φ_s areas by line intervals that can meet three, and only three, at a time and that must meet in such a way that all angles are less than 180°?

By definition, basic forms are different if they *cannot* be made to coincide by one or more of the following processes:

1. Changing the shape of the basic form in any way that does not result in making new line-interval connections or in breaking old ones.
2. Changing the position of the basic form in its plane by translation, rotation, inversion, or reflection.

The derivation of basic forms is greatly facilitated by the use of Dual networks, a geometrical device defined in figure 2 and table 2. Figure 2a shows a unary basic form; figure 2c the corresponding Dual network; and figure 2b the superposition of both. For each basic form, there exists a unique Dual network. In addition, the elements of the two are related by a one–to–one correspondence such that areas correspond to points and line intervals to line segments (see

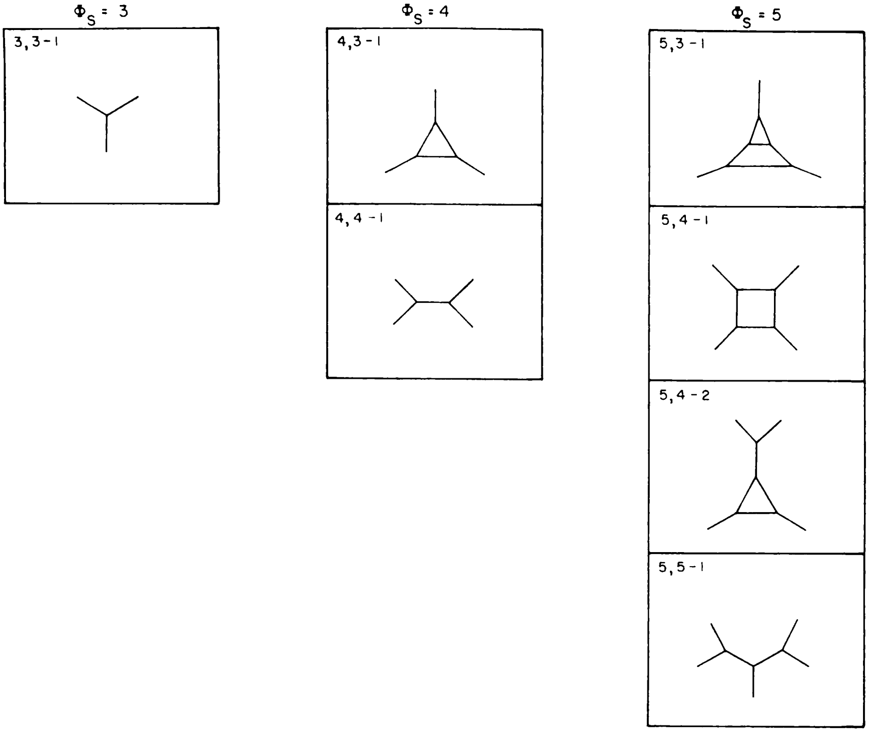


Fig. 7. Unary basic forms for 3, 4, and 5 stable phases. The numerical designation of a basic form is that of the corresponding Dual network.

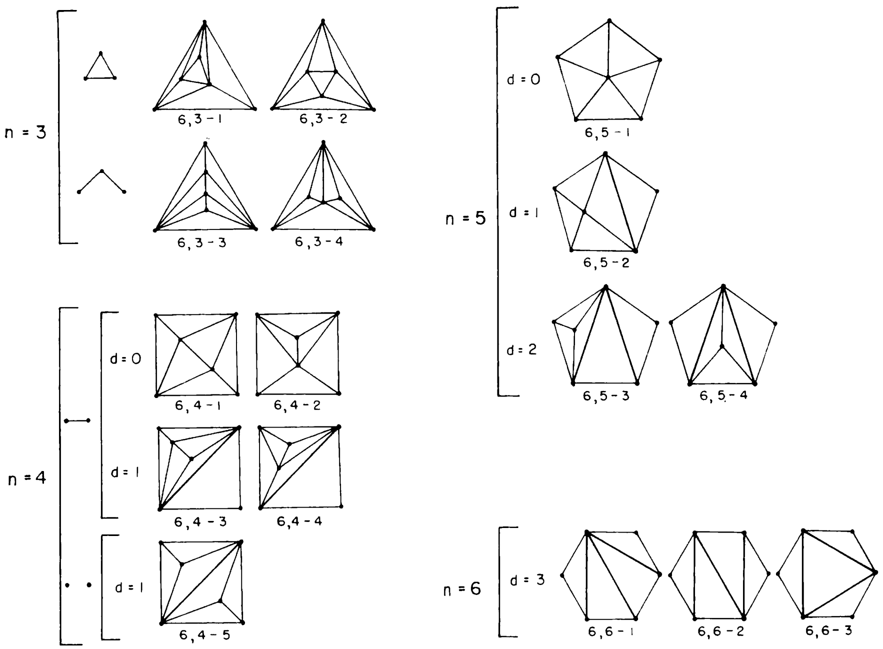


Fig. 8. Dual networks for 6 stable phases. The symbols are the same as in figure 6. Dual networks for a given n are arranged first according to the type of insert (see 4, below) and then according to the number of diagonals d.

table 2). Thus we can derive all the possible Dual networks for a given Φ_s and then convert them to basic forms.

The former process is essentially that of determining the various ways of inserting $\Phi_s - n$ points into a polygon of n sides so as to divide the polygon completely into triangles. The connecting line segments cannot meet or intersect except at one of the original Φ_s points. More specifically:

1. Draw the $\Phi_s - 2$ polygons that have from 3 to Φ_s outside points $(3 \leqslant n \leqslant \Phi_s)$. For $\Phi_s = 6$, for instance, the polygons are a triangle, a square, a pentagon, and a hexagon.
2. Determine all the possible ways of inserting diagonals into each of these n–sided polygons, allowing the number of diagonals (d) to vary from 0 to n–3. These partial networks will be referred to as *frames*. The various possibilities for a hexagon (n = 6) are shown in figure 3.
3. Determine all the possible ways of inserting the $\Phi_s - n$ remaining points into the above frames so as to divide the polygons entirely into triangles (see fig. 4).
4. Whenever there is more than one point to be inserted into a polygon, determine first the various ways of connecting these inserted points to each other (we shall refer to the resulting units as *inserts*) and then the various ways of connecting these inserts to each frame (see fig. 5).

All the possible Dual networks for $3 \leqslant \Phi_s \leqslant 7$ are shown in figures 6, 8, and 10, and the corresponding unary basic forms in figures 7, 9, and 11. Both networks and forms have been numbered according to the scheme: Φ_s, n – arbitrary number. The arbitrary numbers show the order in which the Dual networks were derived, and each basic form has the same arbitrary number as its corresponding Dual network. For the case in which $\Phi_s = 7$ and $n = 3$, the basic forms have been oriented in the same manner as the Dual networks in order to aid comparisons between the two. In most other cases, however, the basic forms have been oriented so as to aid in comparing them with each other.

There are, in general, two methods for converting Dual networks to basic forms. The first of these is faster for simple forms, and the second is easier for complicated forms.

METHOD I (SEE FIGURE 12a)

1. Place a triple point in each triangle of the Dual network.
2. Connect all pairs of these points that have only a single Dual line segment separating them.
3. Draw a perpendicular ray through each outside line segment of the basic polygon. These perpendiculars must originate at a triple point and may cross only one Dual line segment.
4. Redraw the figure, if necessary, so that all angles are less than 180°.

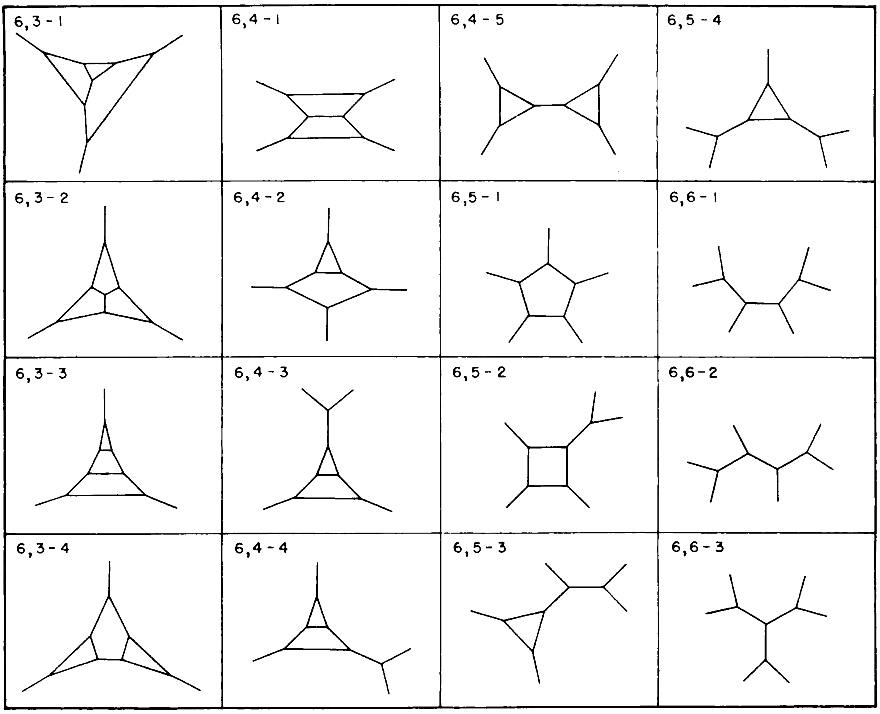


Fig. 9. Unary basic forms for 6 stable phases. The symbols are the same as in figure 7.

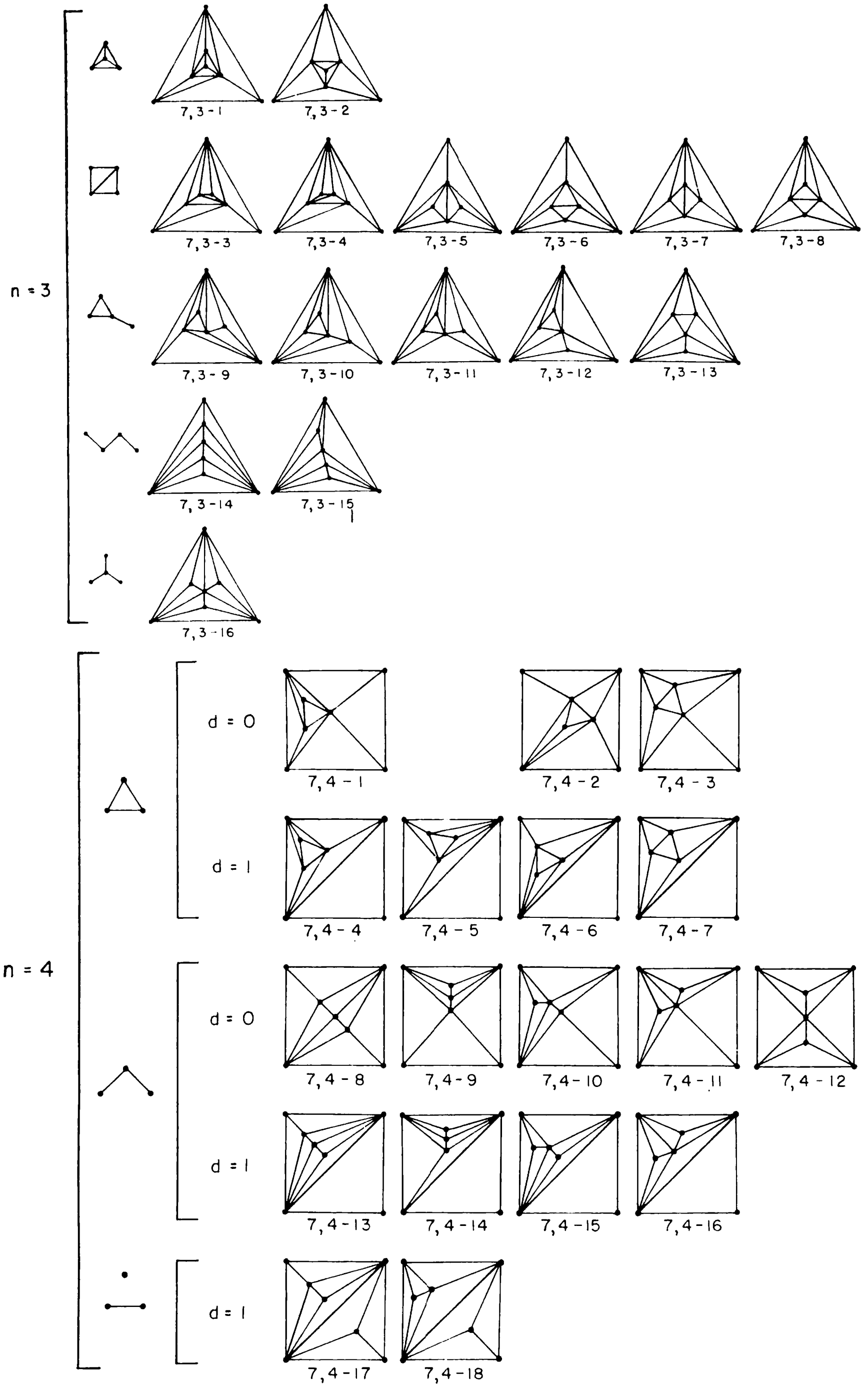
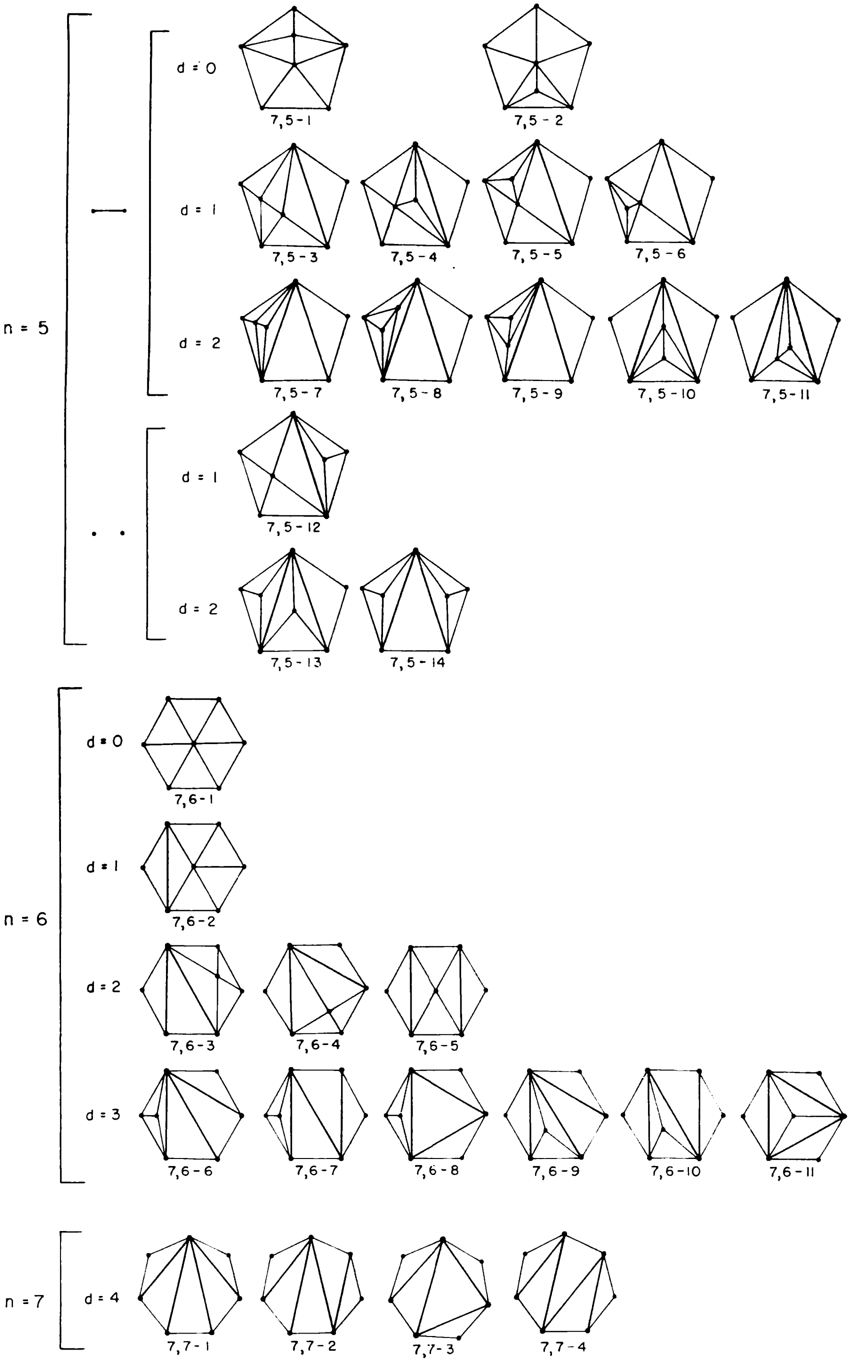


Fig. 10. Dual networks for 7 stable phases.



The symbols are the same as in figure 6.

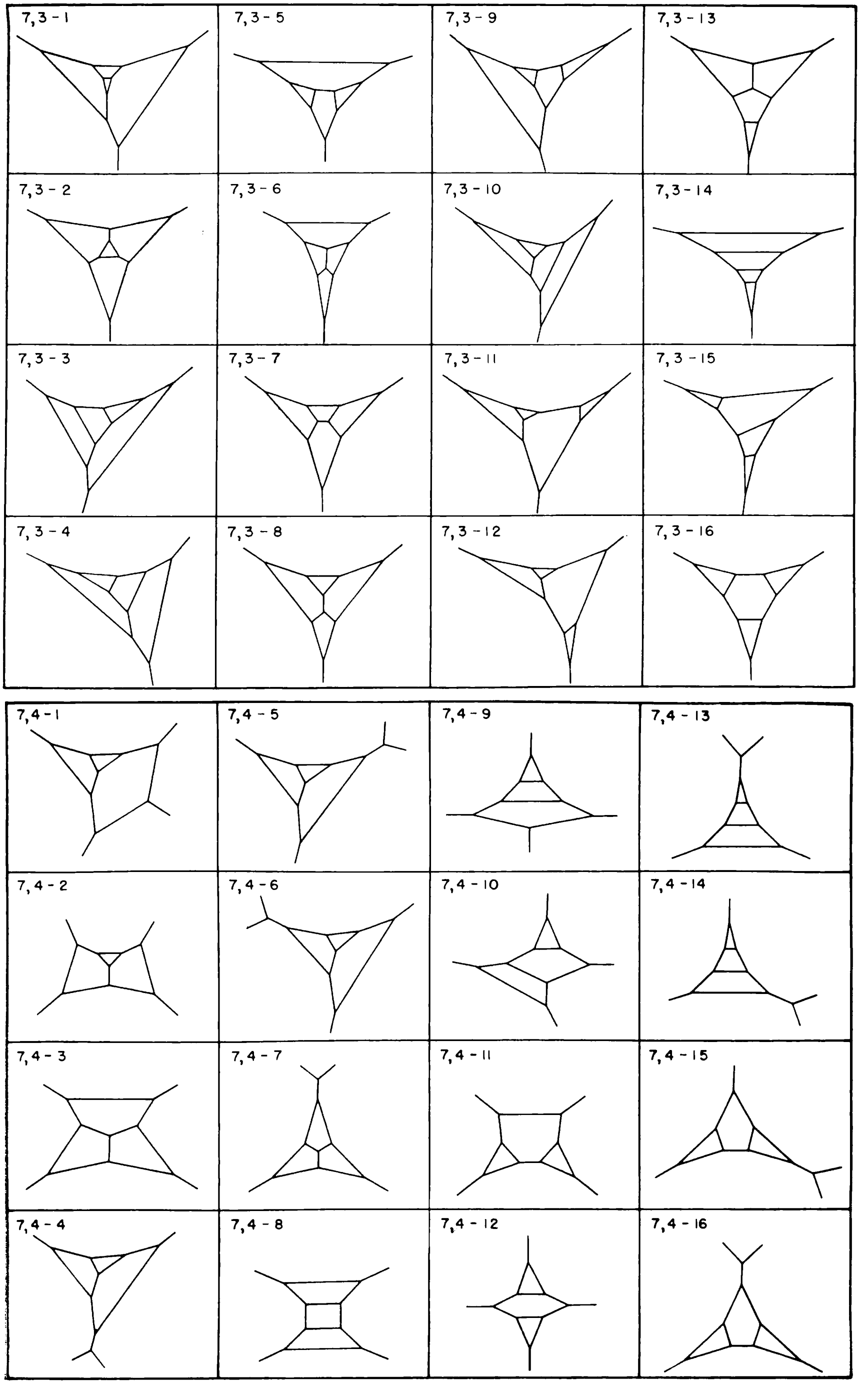
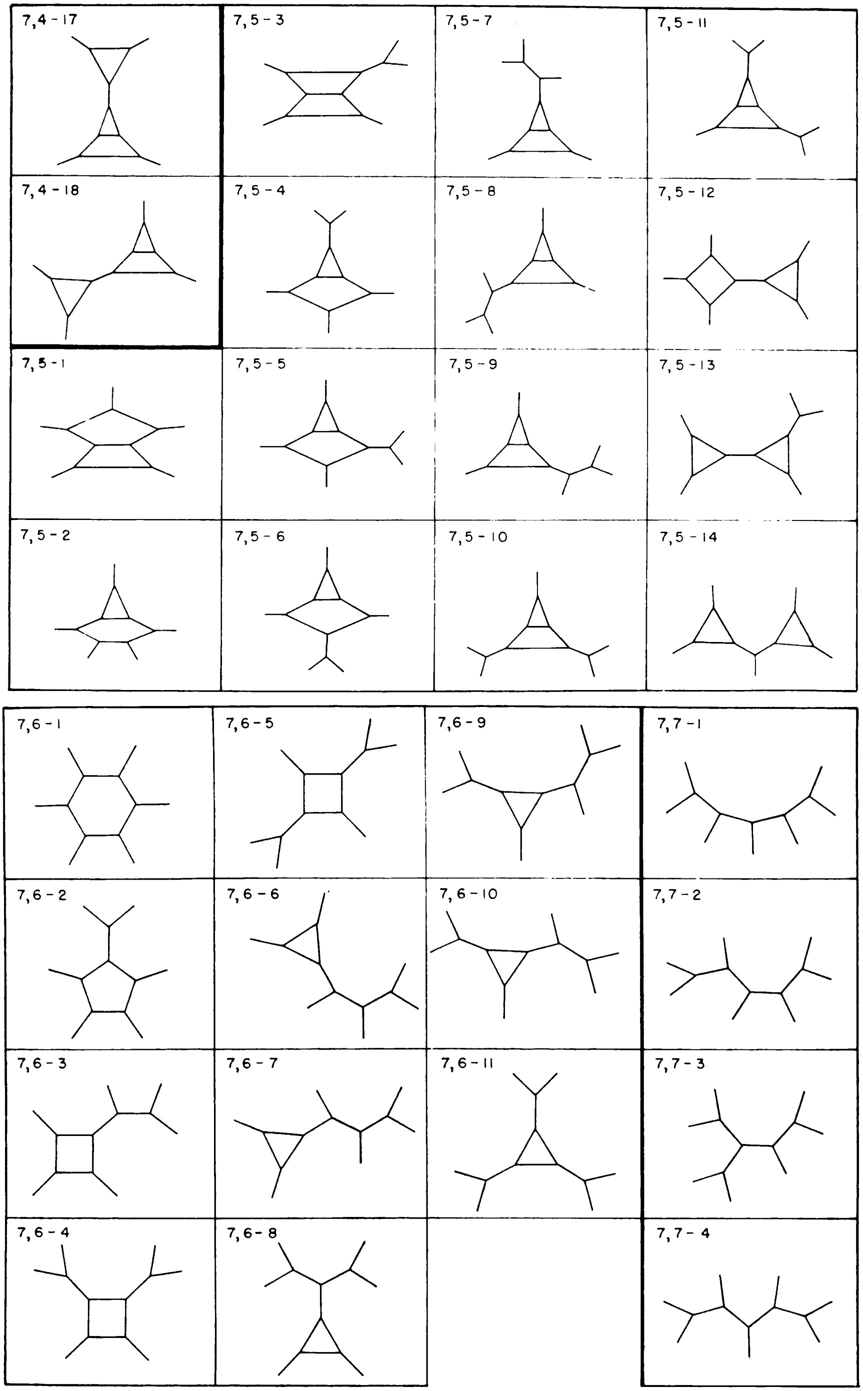


Fig. 11. Unary basic forms for 7 stable phases.



The symbols are the same as in figure 7.

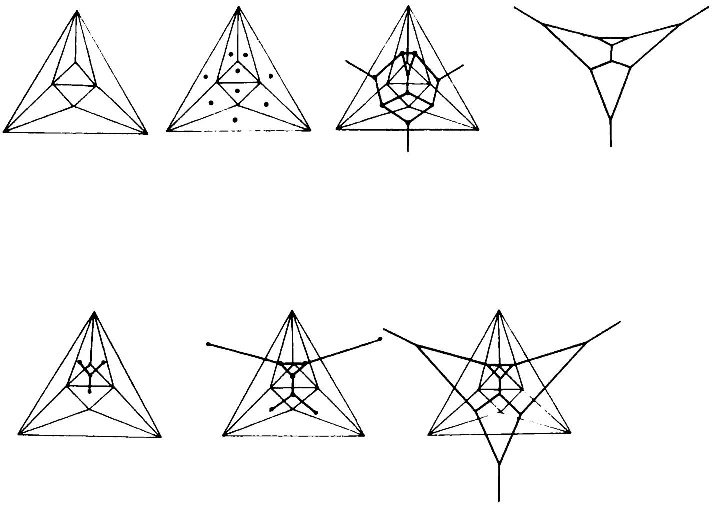


Fig. 12. Methods for converting Dual networks to unary basic forms. For explanation see p. 437, 443.

TABLE 3

Φ_s $E_s\binom{\Phi}{1}$	$E_s\binom{\Phi}{3}$ $D_{B,n}$ $E_s\binom{\Phi}{2}$							$E\binom{\Phi}{3}$ D_B $E\binom{\Phi}{2}$
	n							
	3	4	5	6	7	8	9	
3	1 1 3							1 1 3
4	3 1 6	2 1 5						4 2 6
5	5 1 9	4 2 8	3 1 7					10 4 10
6	7 4 12	6 5 11	5 4 10	4 3 9				20 16 15
7	9 16 15	8 18 14	7 14 13	6 11 12	5 4 11			35 63 21
8	11 78 18	10 88 17	9 69 16	8 53 15	7 28 14	6 12 13		56 328 28
9	13 465 21	12 489 20	11 396 19	10 292 18	9 178 17	8 91 16	7 27 15	84 1938 36

Number of unary basic forms and numbers of ϕ-phase elements. The meaning of the numbers in each square $E_s\binom{\Phi}{2}$, $D_{B,n}$, and $E_s\binom{\Phi}{3}$ or $E\binom{\Phi}{2}$, D_B, and $E\binom{\Phi}{3}$ is defined by the table headings and explained in table 4.

TABLE 4

Key to symbols used in table 3

Symbol	Definition	Means of determination
$D_{B,n}$	Number of unary basic forms for a given Φ_s and n	Empirical enumeration with the aid of Dual networks
D_B	Number of unary basic forms for a given Φ_s	By definition: $D_B = \sum_{n=3}^{n=\Phi_s} D_{B,n}$
$E_s\begin{pmatrix}\Phi\\3\end{pmatrix}$	Number of stable triple points	Empirical formula $E_s\begin{pmatrix}\Phi\\3\end{pmatrix} = 2(\Phi_s - 1) - n$ (where $3 \leqslant n \leqslant \Phi_s$)
$E\begin{pmatrix}\Phi\\3\end{pmatrix}$	Total number of triple points (stable and metastable)	Formula (4) or table 1 $E\begin{pmatrix}\Phi\\3\end{pmatrix} = \frac{\Phi!}{3!(\Phi-3)!}$
$E_s\begin{pmatrix}\Phi\\2\end{pmatrix}$	Number of stable line intervals (or univariant curves)	Empirical formula $E_s\begin{pmatrix}\Phi\\2\end{pmatrix} = 3(\Phi_s - 1) - n$ (where $3 \leqslant n \leqslant \Phi_s$)
$E\begin{pmatrix}\Phi\\2\end{pmatrix}$	Total number of line intervals (stable and metastable)	Formula (4) or table 1 $E\begin{pmatrix}\Phi\\2\end{pmatrix} = \frac{\Phi!}{2!(\Phi-2)!}$
$E_s\begin{pmatrix}1\\\Phi\end{pmatrix}$	Number of stable phase areas	By definition: $E_s\begin{pmatrix}\Phi\\1\end{pmatrix} = \Phi_s$

METHOD II (SEE FIGURE 12b)

1. Place a triple point in one of the triangles of the Dual network.
2. Draw perpendiculars from this point through the three sides of the triangle and terminate them, if practical, in the adjacent triangles. Place triple points at these terminations.
3. Draw perpendiculars from these new points through the remaining sides of their triangles and terminate them, if practical, at triple points in the adjacent triangles.
4. Continue this process until the basic form is complete. If it is necessary to extend any of the perpendiculars past the adjacent triangle, draw the line intervals from its point of termination as though the point were located in the adjacent triangle. Of course, line intervals drawn perpendicular to the outside line segments of the Dual network do not terminate at all.

The numerical results obtained from the preceding derivation of unary basic forms are tabulated in table 3 and explained in table 4. Phase diagrams are derived from these basic forms by designating the liquid + vapor curve and terminating it at a critical point, by orienting the diagram so that the critical point lies on the high-pressure, high-temperature side of the SLV triple point, by curving the line intervals where necessary, and by inserting the limits for pressure ($P \geqslant 0$ bars) and temperature ($T \geqslant 0°$ K). This last process may result in the elimination of portions of the basic form by the P and/or the T axis. Thus triple points that exist in a basic form might not occur in a particular phase diagram, and converging univariant curves may terminate at $P = 0$ and/or $T = 0$ before they intersect. The system SiO_2 (see Boyd and England, 1960) offers a good example. Although the basic form of this diagram (considering only the phases α–quartz, β–quartz, tridymite, cristobalite, coesite, and liquid) is either 6, 4-2, or 6, 5-1, the triple point α-quartz + β-quartz + tridymite does not occur in the phase diagram.

Dual networks can be used to derive all the basic forms for any number of stable phases. Solutions for $\Phi_s = 8$ and $\Phi_s = 9$ have been enumerated in table 3. Dual networks are also helpful in cases where the total number of existing phases is known but where the location of only some of the triple points and univariant curves has been determined. Dual networks will then give all those basic forms that conform with the existing information.

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REFERENCES

Bakhuis Roozeboom, H. W., 1901, 1904, Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre (Erstes Heft, 1901; Zweites Heft, 1904): Braunschweig, Verlag Vieweg, 221, 467 p.

Boyd, F. R., and England, J. L., 1960, The quartz-coesite transition: Jour. Geophys. Research, v. 65, p. 749-756.

Darken, L. S., and Gurry, R. W., 1953, Physical chemistry of metals: New York, McGraw-Hill, 535 p.

Gibbs, J. W., 1928, Collected works, v. I, Thermodynamics: New Haven, Conn., Yale Univ. Press, 434 p.

Greig, J. W., 1955, *in* Carnegie Inst. of Washington Year Book 54, p. 132.

Korzhinskii, D. S., 1959, Physiocochemical basis of the analysis of the paragenesis of minerals: New York, Consultants Bureau, 143 p.

Palatnik, L. S., and Landau, A. I., 1964, Phase Equilibria in Multicomponent Systems (translated by Scripta Technica, Inc.): New York, Holt, Rinehart and Winston, 454 p.

Schreinemakers, F. A. H., 1911, 1913, Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre, Drittes Heft (I, 1911; II, 1913): Braunschweig, Verlag Vieweg, 312, 348 p.

Zharikov, V. A., 1961, Problems of the general theory of multi-system equilibrium diagrams; I, Univariant ($n = -1$) multi-systems (in Russian), *in* Physico-chemical problems of the formation of rocks and ores (Korzhinskii volume): Moscow, Akad. Nauk SSSR, p. 56-77 (English summ.).