# PHASE DIAGRAMS

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A phase is a structurally homogeneous portion of matter. Regardless of the number of chemical constituents of a gas, there is only one vapor phase. This is true also for the liquid form of a pure substance, although a mixture of several liquid substances may exist as one or several phases, depending on the interactions among the substances. On the other hand a pure solid may exist in several phases at different temperatures and pressures because of differences in crystal structure (Reference 1). At the phase transition temperature,  $T_{u'}$ , the chemical composition of the solid remains the same, but a change in the physical properties often will take place. Such changes are found in ferroelectric crystals (example BaTiO<sub>3</sub>) that develop a spontaneous polarization below  $T_{u'}$ , in superconductors (example Pb) that lose all electrical resistance below the transition point, and in many other classes of solids.

In quite a few cases it is difficult to bring about the phase transition, and the high- (or low-) temperature phase persists in its metastable form. Many liquids remain in the liquid state for shorter or longer periods of time when cooled below the melting point (supercooling). However, often the slightest disturbance will cause solidification. Persistence of the high temperature phase in solid– solid transitions is usually of much longer duration. An example of this behavior is found in white tin; although gray tin is the thermodynamically stable form below  $T_{\rm tr}$  (286.4 K), the metal remains in its undercooled, white tin state all the way to T = 0 K, and crystals of gray tin are very difficult to produce.

A *phase diagram* is a map that indicates the areas of stability of the various phases as a function of external conditions (temperature and pressure). Pure materials, such as mercury, helium, water, and methyl alcohol are considered one-component systems and they have *unary* phase diagrams. The equilibrium phases in two-component systems are presented in *binary* phase diagrams. Because many important materials consist of three, four, and more components, many attempts have been made to deduce their multicomponent phase diagrams. However, the vast majority of systems with three or more components are very complex, and no overall maps of the phase relationships have been worked out.

It has been shown during the last 20 to 25 years that very useful partial phase diagrams of complex systems can be obtained by means of thermodynamic modeling (References 2, 3). Especially for complicated, multicomponent alloy systems the CALPHAD method has proved to be a successful approach for producing valuable portions of very intricate phase diagrams (Reference 4). With this method thermodynamic descriptions of the free energy functions of various phases are obtained that are consistent with existing (binary) phase diagram information and other thermodynamic data. Extrapolation methods are then used to extend the thermodynamic functions into a ternary system. Comparison of the results of this procedure with available experimental data is then used to fine-tune the phase diagram and add ternary interaction functions if necessary. In principle this approximation strategy can be extended to four, five, and more component systems.

The nearly two dozen phase diagrams shown below present the reader with examples of some important types of single and multicomponent systems, especially for ceramics and metal alloys. This makes it possible to draw attention to certain features like the kinetic aspects of phase transitions (see Figure 22, which presents a time–temperature–transformation, or TTT, diagram for the precipitation of  $\alpha$ -phase particles from the  $\beta$ -phase in a Ti-Mo alloy; Reference 1, pp. 358–360). The general references listed below and the references to individual figures contain phase diagrams for many additional systems.

### **General References**

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- 7. Roth. R. S., Ed., *Phase Diagrams for Ceramists*, Vol. I (1964) to Volume XI (1995), American Ceramic Society, Waterville, OH.

# **References to Individual Phase Diagrams**

- Figure 1. Carbon: Reference 7, Vol. X (1994), Figure 8930. Reprinted with permission.
- Figure 2. Si-Ge : Ref. 5, p. 2.231. Reprinted with permission.
- Figure 3. H<sub>2</sub>O (ice): See figure.
- Figure 4.  $\tilde{SiO}_2$ : Reference 7, Vol. XI (1995), Figure 9174. Reprinted with permission.
- Figure 5. Fe-O: Darken, L.S., and Gurry, R.W., *J. Am. Chem. Soc.*, 68, 798, 1946. Reprinted with permission.
- Figure 6. Ti-O: Reference 5, p. 2.324. Reprinted with permission.
- Figure 7. BaO-TiO<sub>2</sub>: Reference 7, Vol. III (1975), Figure 4302. Reprinted with permission.
- Figure 8. MgO-Al<sub>2</sub>O<sub>3</sub>: Reference 7, Vol. XI (1995), Figure 9239. Reprinted with permission.
- Figure 9.  $Y_2O_3$ -ZrO<sub>2</sub>: Reference 7, Vol. XI (1995), Figure 9348. Reprinted with permission.
- Figure 10. Si-N-Al-O (Sialon): Reference 7, Vol. X (1994), Figure 8759. Reprinted with permission.
- Figure 11. PbO-ZrO<sub>2</sub>-TiO<sub>2</sub> (PZT): Reference 7, Vol. III (1975), Figure 4587. Reprinted with permission.
- Figure 12. Al-Si-Ca-O: Reference 7 (1964), Vol. I, Figure 630. Reprinted with permission.
- Figure 13. Y-Ba-Cu-O: Whitler, J.D., and Roth, R.S., *Phase Diagrams for High T<sub>c</sub> Superconductors*, Figure S-082, American Ceramic Society, Waterville, OH, 1990. Reprinted with permission.
- Figure 14. Al-Cu: Reference 5, p. 2.44. Reprinted with permission.
- Figure 15. Fe-C: Ralls, K.M., Courtney, T.H., and Wulff, J., Introduction to Materials Science and Engineering, Figure 16.13, John Wiley & Sons, New York, 1976. Reprinted with permission.
- Figure 16. Fe-Cr: Reference 5, p. 2.152. Reprinted with permission.
- Figure 17. Cu-Sn: Reference 5, p. 2.178. Reprinted with permission.
- Figure 18. Cu-Ni: Reference 5, p. 2.173. Reprinted with permission.
- Figure 19. Pb-Sn (solder): Reference 5, p. 2.335. Reprinted with permission.
- Figure 20. Cu-Zn (brass): Subramanian, P.R., Chakrabarti, D.J., and Laughlin, D.E., Eds., *Phase Diagrams of Binary Copper Alloys*, p. 487, ASM International, Materials Park, OH, 1994. Reprinted with permission.
- Figure 21. Co-Sm: Reference 5, p. 2.148. Reprinted with permission.
- Figure 22. Ti-Mo: Reference 5, p. 2.296; Reference 1, p. 359. Reprinted with permission.
- Figure 23. Fe-Cr-Ni: Reference 5, Figure 48. Reprinted with permission.



 $\label{eq:FIGURE 1.} Flagure 1. Phase diagram of carbon. (A) Martensitic transition: hex graphite <math>\rightarrow$  hex diamond. (B) Fast graphite-to-diamond transition. (C) Fast diamond-to-graphite transition.



FIGURE 2. Si-Ge system.

	Composition,	Pearson	Space
Phase	mass % Si	symbol	group
(Ge,Si)	0 to 100	cF8	$Fd\overline{3}m$
High-pressure phases			
GeII	-	tI4	I4 <sub>1</sub> /amd
SiII	-	tI4	$I4_1/amd$



**FIGURE 3.** Diagram of the principal phases of ice. Solid lines are measured boundaries between stable phases; dotted lines are extrapolated. Ice IV is a metastable phase that exists in the region of ice V. Ice IX exists in the region below -100 °C and pressures in the range 200–400 MPa. Ice X exists at pressures above 44 GPa. See Table 1 for the coordinates of the triple points, where liquid water is in equilibrium with two adjacent solid phases.

TABLE 1. Crystal Structure, Density, and Transition Temperatures for the Phases of Ice
Crystal

Phase	system	Cell parameters	Z	n	$\rho/g \ cm^{-3}$	<b>Triple points</b>
Ih	Hexagonal	a = 4.513; c = 7352	4	4	0.93	I-III: –21.99 °C, 209.9 MPa
Ic	Cubic	<i>a</i> = 6.35	8	4	0.94	
II	Rhombohedral	$a = 7.78; \alpha = 113.1^{\circ}$	12	4	1.18	
III	Tetragonal	a = 6.73; c = 6.83	12	4	1.15	III-V: –16.99 °C, 350.1 MPa
IV	Rhombohedral	$a = 7.60; \alpha = 70.1^{\circ}$	16	4	1.27	
V	Monoclinic	a = 9.22; b = 7.54,	28	4	1.24	V-VI: 0.16 °C, 632.4 MPa
		$c = 10.35; \beta = 109.2^{\circ}$				
VI	Tetragonal	a = 6.27; c = 5.79	10	4	1.31	VI-VII: 82 °C, 2216 MPa
VII	Cubic	a = 3.41	2	8	1.56	
VIII	Tetragonal	a = 4.80; c = 6.99	8	8	1.56	
IX	Tetragonal	a = 6.73; c = 6.83	12	4	1.16	
Х	Cubic	<i>a</i> = 2.83	2	8	2.51	
VI VII VIII IX X	Tetragonal Cubic Tetragonal Tetragonal Cubic	a = 5.22, b = 7.94, $c = 10.35; \beta = 109.2^{\circ}$ a = 6.27; c = 5.79 a = 3.41 a = 4.80; c = 6.99 a = 6.73; c = 6.83 a = 2.83	10 2 8 12 2	4 8 8 4 8	1.24 1.31 1.56 1.56 1.16 2.51	VI-VII: 82 °C, 2216 MPa

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- 2. Lerner, R.G. and Trigg, G.L., Eds., *Encyclopedia of Physics*, VCH Publishers, New York, 1990.
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**FIGURE 4.** SiO<sub>2</sub> system. Crist = cristobalite; Trid = tridymite.





Point	$t/^{\circ}C$	% O	$p_{\rm co}/p_{\rm co}$	Point	t/°C	% O	$p_{\rm co}/p_{\rm co}$	$p_{0}/atm$
Α	1539		002 00	Q	560	23.26	1.05	02
В	1528	0.16	0.209	R	1583	28.30		1
С	1528	22.60	0.209	R'	1583	28.07		1
G	1400ª	22.84	0.263	S	1424	27.64	16.2	
Н	1424	25.60	16.2	V	1597	27.64		0.0575
Ι	1424	25.31	16.2	Y	1457	28.36		1
J	1371	23.16	0.282	Ζ	1457	30.04		1
L	911ª	23.10	0.447	Z'		30.6		
Ν	1371	22.91	0.282					

<sup>a</sup> Values for pure iron.





	Composition,	Pearson	Space
Phase	mass % O	symbol	group
(βTi)	0 to 3	cI2	Im3m
(aTi)	0 to 13.5	hP2	P63/mmc
Ti <sub>3</sub> O	~8 to ~13	$hP \sim 16$	$P\bar{3}c$
Ti <sub>2</sub> O	~10 to 14.4	hP3	$P\bar{3}m1$
γŤiO	15.2 to 29.4	cF8	Fm3m
Ti <sub>2</sub> O <sub>2</sub>	~18	$hP\sim5$	P6/mmm
βŤiŌ	~24 to ~29.4	<i>C</i> **	-
αΤίΟ	~25.0	mC16	A2/m or B*/*
βTi <sub>1-x</sub> O	~29.5	oI12	<i>I</i> 222
αTi <sub>1</sub> O	~29.5	<i>tI</i> 18	I4/m
βTi <sub>2</sub> O <sub>3</sub>	33.2 to 33.6	hR30	$R\bar{3}c$
αTi <sub>2</sub> O <sub>3</sub>	33.2 to 33.6	hR30	$R\bar{3}c$
βTi <sub>2</sub> O <sub>5</sub>	35.8	$m^{**}$	-
αTi <sub>3</sub> O <sub>5</sub>	35.8	mC32	C2/m
α´Ti <sub>2</sub> O <sub>5</sub>	35.8	mC32	Cc
γTi <sub>4</sub> O <sub>7</sub>	36.9	aP44	$P\bar{1}$
βTi <sub>4</sub> O <sub>7</sub>	36.9	aP44	$P\bar{1}$
αTi4O <sub>7</sub>	36.9	aP44	$P\bar{1}$
γTi <sub>5</sub> O <sub>9</sub>	37.6	aP28	$P\bar{1}$
βTi <sub>6</sub> O <sub>11</sub>	38.0	aC68	AĪ
Ti <sub>2</sub> O <sub>13</sub>	38.3	aP40	$P\bar{1}$
Ti <sub>8</sub> O <sub>15</sub>	38.5	aC92	AĪ
Ti <sub>9</sub> O <sub>17</sub>	38.7	aP52	$P\overline{1}$
Rutile TiO <sub>2</sub>	40.1	tP6	$P4_2/mnm$
Metastable phases			-
Anatase	_	<i>tI</i> 12	I4,/amd
Brookite	_	oP24	Pbca
High-pressure phases			
TiO <sub>2</sub> -II	_	oP12	Pbcn
TiO <sub>2</sub> -III	_	$hP{\sim}48$	-
-			







**FIGURE 9.**  $Y_2O_3$ - $ZrO_2$  system.  $C_{ss}$  = cubic  $ZrO_2$  ss (fluorite-type ss);  $Y_{ss}$  = cubic  $Y_2O_3$  ss;  $Tet_{ss}$  = tetragonal  $ZrO_2$  ss;  $Mon_{ss}$  = monoclinic  $ZrO_2$  ss;  $H_{ss}$  = hexagonal  $Y_2O_3$  ss;  $3:4 = Zr_3Y_4O_{12}$ ;  $1:6 = ZrY_6O_{11}$  ss.



FIGURE 10.  $3(SiO_2)-Si_3N_4-4(AIN)-2(Al_2O_3)$  system. "Behavior" diagram at 1700 °C. The labels 8H, 15R, 12H, 21R, 27R, 2H<sup>δ</sup> indicate defect AlN polytypes. β' = 3-sialon (Si<sub>6-x</sub>Al\_xO\_xN\_8-x); O' = sialon of Si<sub>2</sub>ON<sub>2</sub> type; X = SiAlO<sub>2</sub>N ("nitrogen mullite"). ALON ss = aluminum oxynitride ss extending from approximately Al<sub>2</sub>O<sub>9</sub>N to Al<sub>3</sub>O<sub>3</sub>N.



**FIGURE 11.** PbO-ZrO<sub>2</sub>-TiO<sub>2</sub> (PZT) system, subsolidus at 1100 °C. P = PbO;  $T = TiO_2$ ;  $Z = ZrO_2$ .



**FIGURE 12.** CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system (temperatures in  $^{\circ}$ C).

### **Crystalline Phases**

Notation	Oxide formula
Cristobalite }	SiO <sub>2</sub>
Tridymite	
Pseudowollastonite	CaO-SiO <sub>2</sub>
Rankinite	3CaO-2SiO <sub>2</sub>
Lime	CaO
Corundum	Al <sub>2</sub> O <sub>3</sub>
Mullite	3Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>
Anorthite	CaO·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>
Gehlenite	2CaO·Al <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub>

Temperatures up to approximately 1550  $^\circ\rm C$  are on the Geophysical Laboratory Scale; those above 1550  $^\circ\rm C$  are on the 1948 International Scale.



**FIGURE 13.** BaO-Y<sub>2</sub>O<sub>3</sub>-CuO system. 2:1:3 = Ba<sub>2</sub>YCu<sub>3</sub>O<sub>7-x</sub>; 1:2:1 = BaY<sub>2</sub>CuO<sub>5</sub>; 4:1:2 = Ba<sub>4</sub>YCu<sub>2</sub>O<sub>7.5+x</sub>; and 5:1:3 = Ba<sub>5</sub>YCu<sub>3</sub>O<sub>9.5+x</sub>. The superconducting 2:1:3 phase was prepared using barium peroxide.



FIGURE 14. Al-Cu system.

	Composition,	Pearson	Space
Phase	wt % Cu	symbol	group
(Al)	0 to 5.65	cF4	Fm3m
θ	52.5 to 53.7	<i>tI</i> 12	I4/mcm
η,	70.0 to 72.2	<i>oP</i> 16 or <i>oC</i> 16	Pban or Cmmm
$\eta_2$	70.0 to 72.1	<i>mC</i> 20	C2/m
$\zeta_1$	74.4 to 77.8	hP42	P6/mmm
$\zeta_2$	74.4 to 75.2	(a)	-
ε	77.5 to 79.4	(b)	-
ε,	72.2 to 78.7	hP4	P63/mmc
δ	77.4 to 78.3	(c)	R3m
$\gamma_0$	77.8 to 84	(d)	-
γ <sub>1</sub>	79.7 to 84	cP52	$P\bar{4}3m$
β	83.1 to 84.7	(d)	-
β	85.0 to 91.5	cI2	Im3m
α <sub>2</sub>	88.5 to 89	(e)	-
(Cu)	90.6 to 100	cF4	Fm3m
Metastable phases			
θ´	_	tP6	-
β´	_	<i>cF</i> 16	Fm3m
Al <sub>3</sub> Cu <sub>2</sub>	61 to 70	hp5	$P\bar{3}m1$

(a) Monoclinic? (b) Cubic? (c) Rhombohedral. (d) Unknown. (e)  $\mathrm{D0}_{_{22}}\text{-type}$  long-period superlattice.





	Composition,	Pearson	Space
Phase	mass % C	symbol	group
(δFe)	0 to 0.09	cI2	Im3m
(yFe)	0 to 2.1	cF4	Fm3m
(aFe)	0 to 0.021	cI2	Im3m
(C)	100	hP4	P6 <sub>3</sub> /mmc
Metastable/high-pressur	e phases		-
(ɛFe)	0	hP2	P6 <sub>3</sub> /mmc
Martensite	< 2.1	tI4	I4/mmm
Fe <sub>4</sub> C	5.1	cP5	P43m
$Fe_{3}C(\theta)$	6.7	oP16	Рпта
$Fe_5C_2(\chi)$	7.9	mC28	C2/c
Fe <sub>7</sub> C <sub>3</sub>	8.4	hP20	$P6_{3}mc$
Fe <sub>2</sub> C <sub>3</sub>	8.4	oP40	Pnma
$Fe_2C(\eta)$	9.7	<i>oP</i> 6	Pnnm
$Fe_2C(\epsilon)$	9.7	$hP^*$	P6,22
Fe <sub>2</sub> C	9.7	$hP^*$	P3m1
$(\overline{C})$	100	cF8	Fd3m



FIGURE 16. Fe-Cr system.

	Composition,	Pearson	Space
Phase	mass % Cr	symbol	group
(aFe, Cr)	0 to 100	cI2	Im3m
(γFe)	0 to 11.2	cF4	Fm3m
σ	42.7 to 48.2	<i>tP</i> 30	$P4_2/mnm$





Phase	Composition, mass % Sn	Pearson symbol	Space group
α	0 to 15.8	cF4	Fm3m
β	22.0 to 27.0	cI2	Im3m
γ	25.5 to 41.5	<i>cF</i> 16	Fm3m
δ	32 to 33	cF416	$F\bar{4}3m$
ζ	32.2 to 35.2	hP26	$P6_{3}$
ε	27.7 to 39.5	oC80	Стст
η	59.0 to 60.9	hP4	P6 <sub>3</sub> /mmc
ή	44.8 to 60.9	(a)	-
(βSn)	~100	tI4	I4 <sub>1</sub> /amd
(aSn)	100	cF8	$Fd\bar{3}m$

(a) Hexagonal; superlattice based on NiAs-type structure.



FIGURE 18. Cu-Ni system.

	Composition,	Pearson	Space
Phase	mass % Ni	symbol	group
(Cu, Ni) (above 354.5 °C)	0 to 100	cF4	$Fm\overline{3}m$



FIGURE 19. Pb-Sn system.

	Composition,	Pearson	Space
Phase	mass % Sn	symbol	group
(Pb)	0 to 18.3	cF4	Fm3m
(βSn)	97.8 to 100	tI4	I4 <sub>1</sub> /amd
(aSn)	100	cF8	Fd3m
High-pressure phases			
ε(a)	52 to 74	hP1	P6/mmm
ε´(b)	52	hP2	$P6_{3}/mmc$

(a) From phase diagram calculated at 2500 MPa. (b) This phase was claimed for alloys at 350  $^\circ C$  and 5500 MPa.





Phase	Composition, mass % Zn	Pearson symbol	Space group
α or (Cu)	0 to 38.95	cF4	Fm3m
β	36.8 to 56.5	cI2	Im3m
β´	45.5 to 50.7	cP2	Pm3m
γ	57.7 to 70.6	cI52	I43m
δ	73.02 to 76.5	hP3	Pē
ε	78.5 to 88.3	hP2	$P6_3/mmc$
η or (Zn)	97.25 to 100	hP2	$P6_3/mmc$



FIGURE 21. Co-Sm system.

Phase	Composition, mass % Sm	Pearson symbol	Space group
(aCo)	0 to ~3.7	cF4	Fm3m
(eCo)	~0	hP2	P6 <sub>3</sub> /mmc
$\beta Co_{17}Sm_2$	~23.0	hP38	P6 <sub>3</sub> /mmc
$\alpha Co_{17}Sm_2$	~23.0	hR19	R3m
		hP8	P6/mmm
$Co_{5+x}Sm$	~33 to 34	-	-
Co <sub>5-x</sub> Sm	~34 to 35	-	-
Co <sub>19</sub> Sm <sub>5</sub>	~40.1	hR24	R3m
		hP48	P6 <sub>3</sub> /mmc
$\alpha Co_7 Sm_2$	~42.1	hR18	R3m
$\beta Co_7 Sm_2$	~42.1	hP36	P6 <sub>3</sub> /mmc
Co <sub>3</sub> Sm	46	hR12	R3m
Co <sub>2</sub> Sm	56.0	hR4	R3m
		cF24	Fd3m
Co <sub>4</sub> Sm <sub>9</sub>	~85.1	0**	-
CoSm <sub>3</sub>	88	oP16	Pnma
(ySm)	~100	cI2	Im3m
(βSm)	~100	hP2	P6 <sub>3</sub> /mmc
(αSm)	~100	hR3	R3m
Other reported phases			
Co <sub>5</sub> Sm	~33.8	hP6	P6/mmm
Co <sub>2</sub> Sm <sub>5</sub>	~86.4	<i>mC</i> 28	C2/c



FIGURE 22. Ti-Mo system.

Phase	Composition, mass % Mo	Pearson symbol	Space group
(βTi, Mo)	0 to 100	cI2	Im3 <sup>m</sup>
(aTi)	0 to 0.8	hP2	P6 <sub>3</sub> /mmc
α´	(a)	hP2	P6 <sub>3</sub> /mmc
α″	(a)	oC4	Стст
ω	(a)	hP3	P6/mmm
(a) Metastable.			



Experimental time–temperature–transformation (TTT) diagram for Ti-Mo. The start and finish times of the isothermal precipitation reaction vary with temperature as a result of the temperature dependence of the nucleation and growth processes. Precipitation is complete, at any temperature, when the equilibrium fraction of  $\alpha$  is established in accordance with the lever rule. The solid horizontal line represents the athermal (or nonthermally activated) martensitic transformation that occurs when the  $\beta$  phase is quenched.



FIGURE 23. The isothermal section at 900 °C (1652 °F) of the iron-chromium-nickel ternary phase diagram, showing the nominal composition of 18-8 stainless steel.