

Topic 5B - Phase Equilibria in One-Component Systems

Phase Changes

Freezing/Melting

Only slightly dependent on pressure. For most solids, increasing pressure causes only slight increase in $T_{m.p.}$

Exception exists for only a few compounds, such as H_2O , for which $\rho_{solid} < \rho_{liquid}$ *

Boiling/Condensation

Boiling occurs throughout liquid, not just at surface.

$T_{b.p.}$ = Temperature at which $P_{v.p.} = 1 \text{ atm.}$

Phase Diagrams

Phase Boundaries (Equilibria)

Solid-Vapor	($P_{v.p.}$ of Solid)
Liquid-Vapor	($P_{v.p.}$ of Liquid)
Solid-Liquid	(Dependence of $T_{m.p.}$ on P)

Triple point(s)
Critical properties

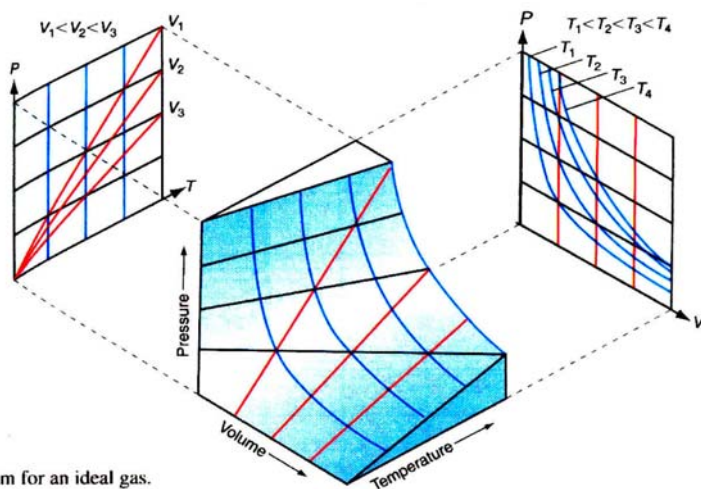


FIGURE 8.12

A P - V - T diagram for an ideal gas. Constant pressure, constant volume, and constant temperature paths are shown as black, red, and blue curves, respectively.

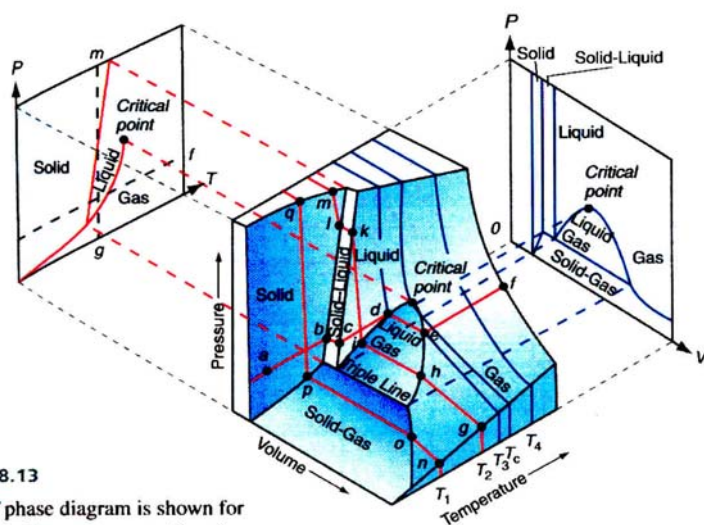


FIGURE 8.13

A P - V - T phase diagram is shown for a substance that contracts on freezing. The indicated processes are discussed in the text.

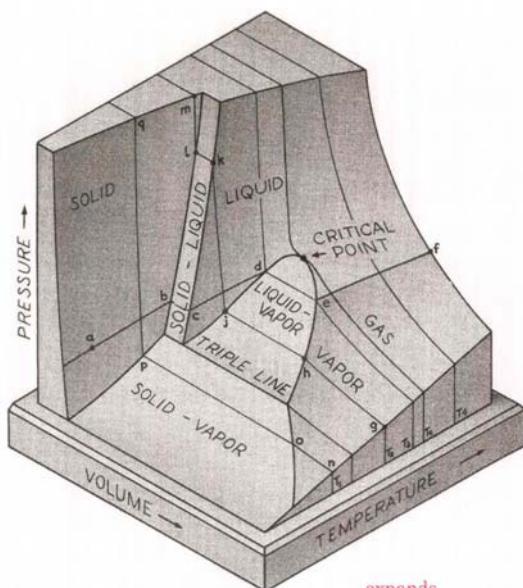


Fig. 18-7. pVT -surface for a substance that ~~contracts~~ **expands** on melting.

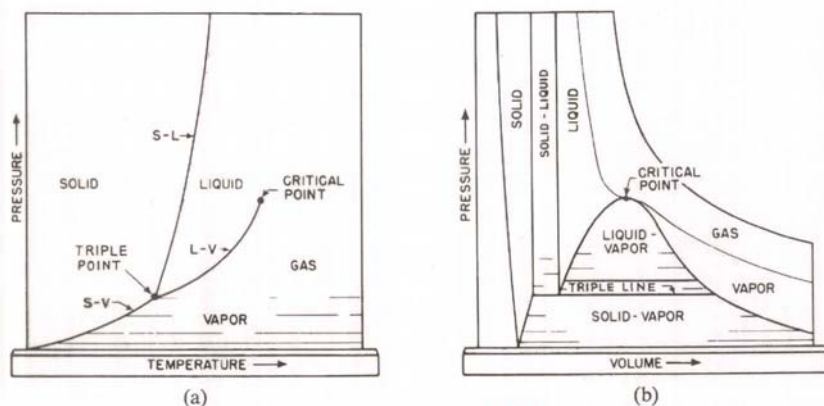


Fig. 18-9. Projections of the surface in Fig. 18-6 on the pT - and pV -planes.

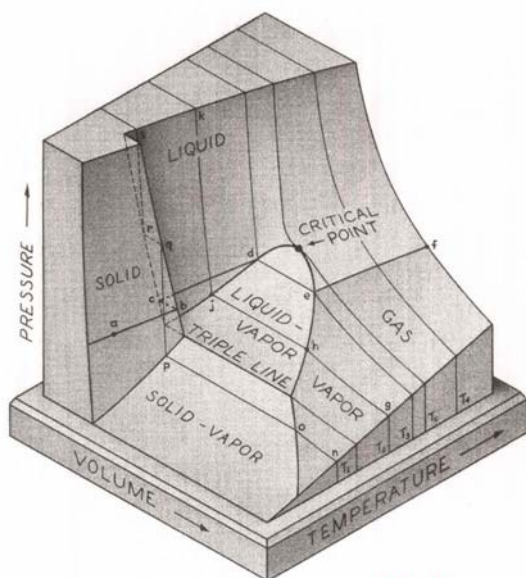


Fig. 18-6. pVT -surface for a substance that **contracts** expands on melting.

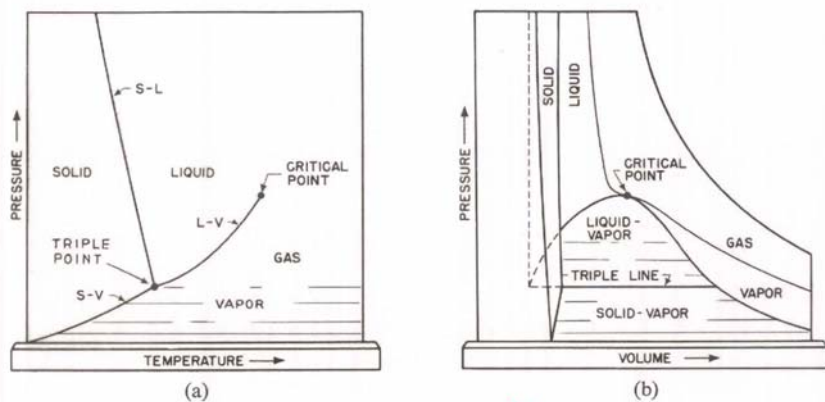


Fig. 18-10. Projections of the surface in Fig. 18-7 on the pT - and pV -planes.

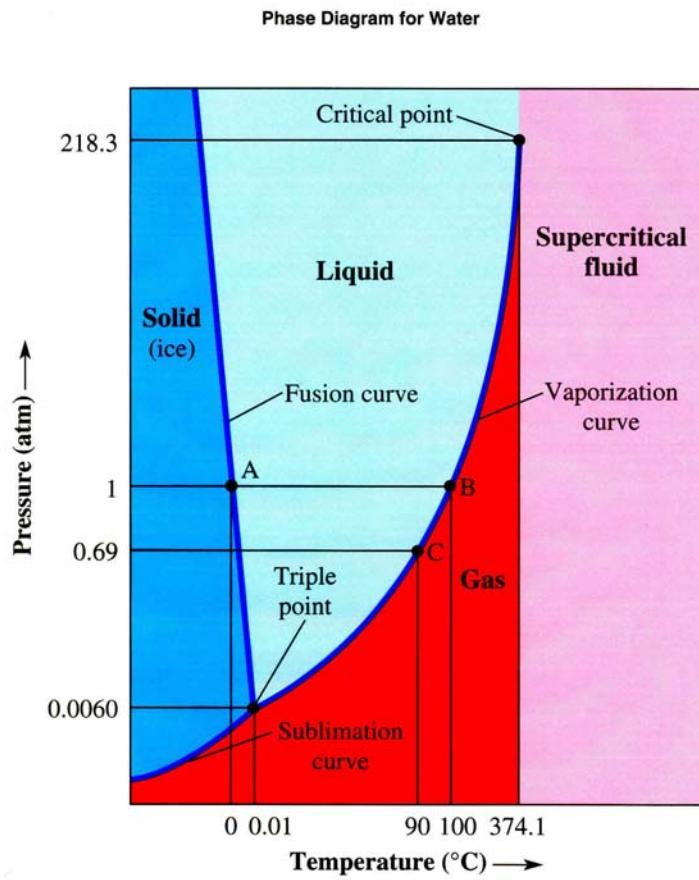
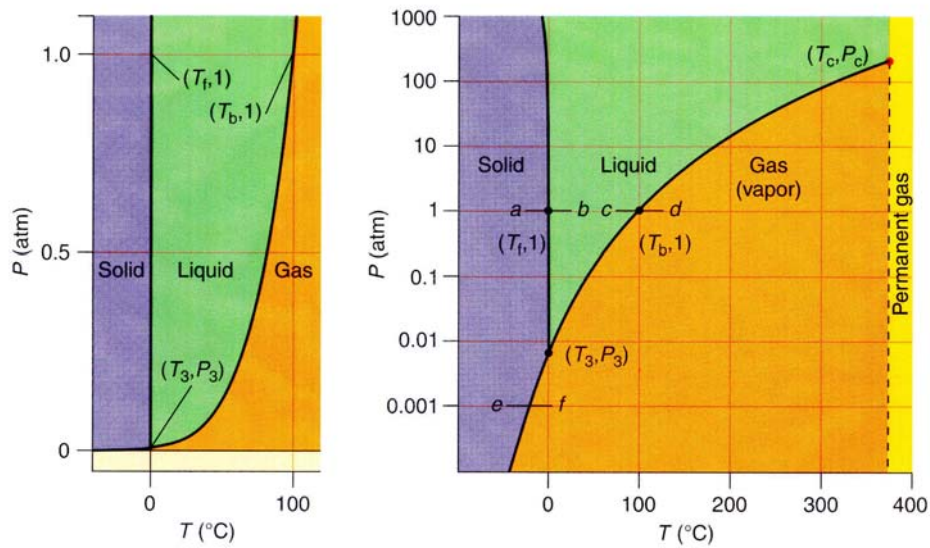


Figure 14.8: The Phase Diagram: Water



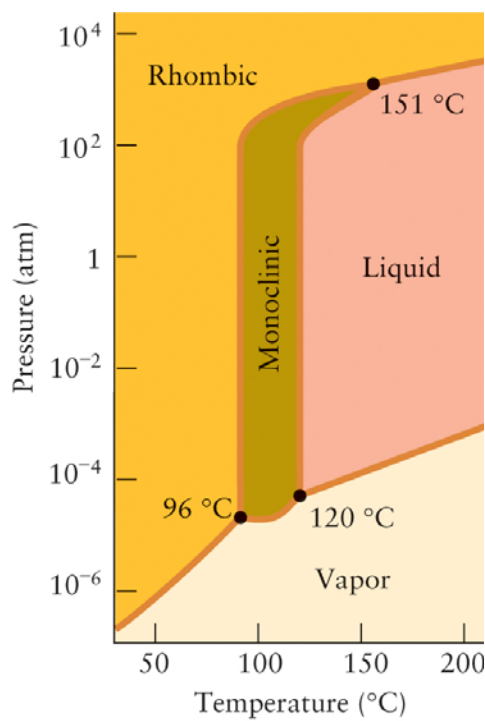
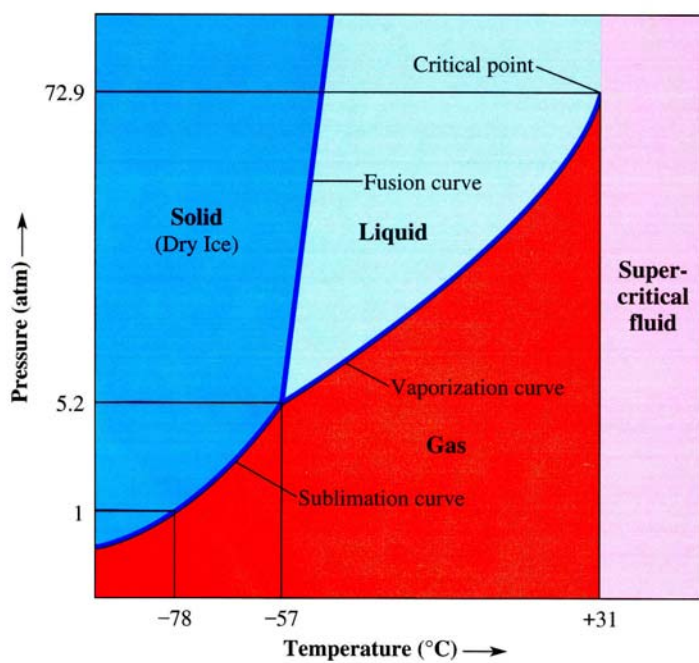
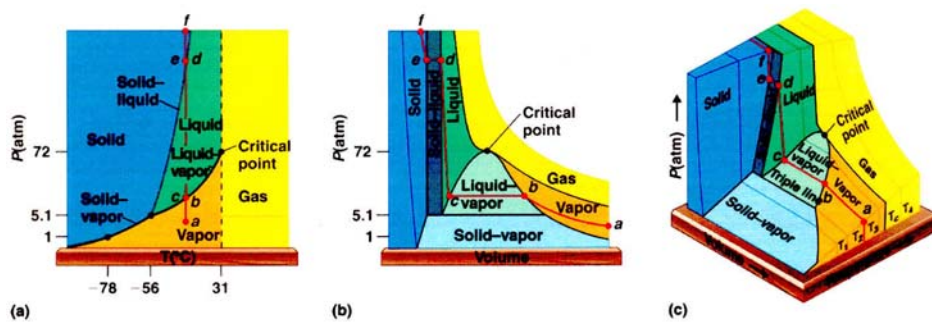


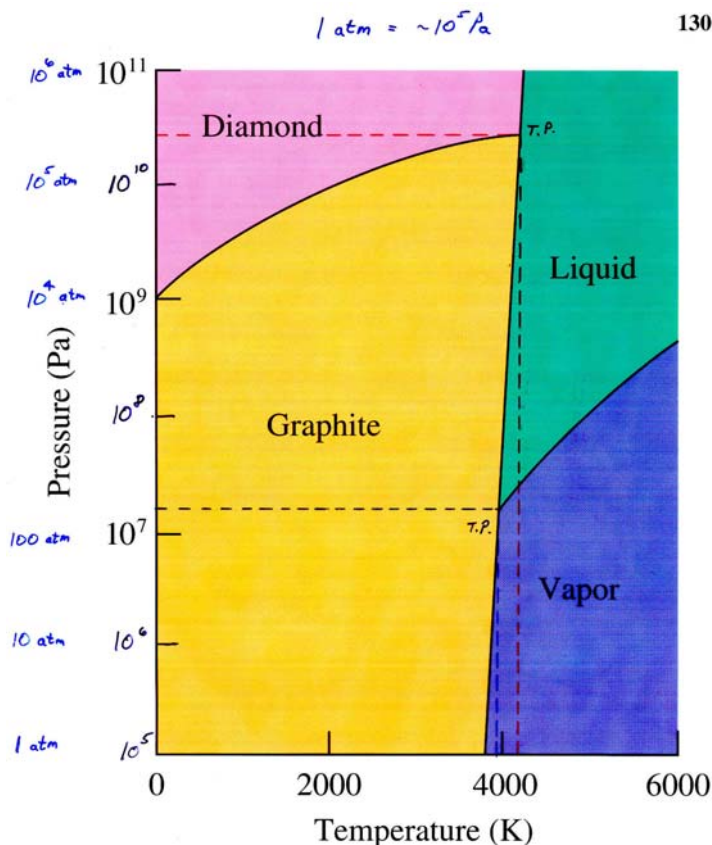
FIGURE 10.9 The phase diagram for sulfur. Notice that there are two solid phases and three triple points. The pressure scale, which is logarithmic, covers a very wide range of values.

Phase Diagram for Carbon Dioxide



**Figure 14.9**

Phase diagrams for carbon dioxide (CO_2). Pressure and temperature scales are nonuniform, schematic only. (a) The normal P versus T phase diagram. CO_2 is one of a small number of substances whose triple point lies above 1 atm; therefore CO_2 does not display normal melting and boiling points, but only a single sublimation point at -78°C . In addition, its critical point occurs at the readily accessible temperature of 31°C . The line af depicts what happens when a CO_2 sample is compressed at constant T , where T lies between T_3 and T_c : first condensation (point bc) and then freezing (point de). Freezing occurs because solid CO_2 (dry ice) is denser than liquid CO_2 , making the liquid–solid equilibrium line slope to the right; freezing does not occur for H_2O under these conditions. (b) P versus V phase diagram for CO_2 ; each phase equilibrium point on the P – T diagram becomes a horizontal line on P versus V , due to the change in V (ΔV) that accompanies a phase change, as illustrated by the path $abcdef$ of (a). The phase transitions bc and de are shown by the heavier lines. The phase boundaries then “fold over” to produce equilibrium areas instead of lines; that for liquid–vapor has a maximum at the critical point. Away from the phase equilibrium curves, constant T defines an isotherm, which becomes that for an ideal gas (a graph of Boyle’s law) as T increases beyond T_c . (c) If the features of (a) and (b) are combined, we obtain a phase surface $P(V,T)$ that summarizes all aspects of phase behavior for a pure substance; the line $abcdef$ is a constant- T cut through this surface.

**Phase diagram for carbon**

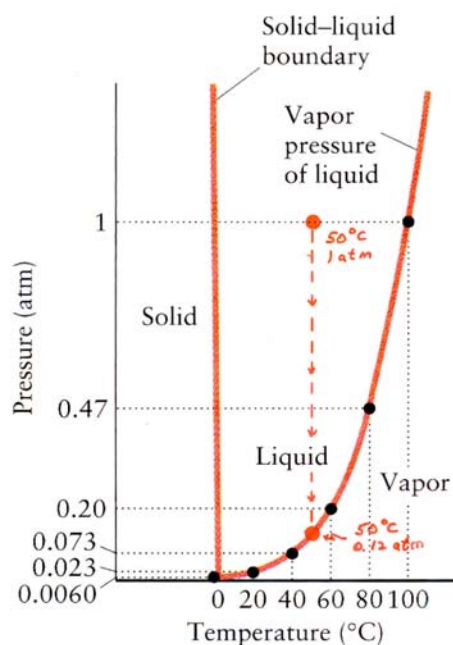


FIGURE 9.10 The liquid–vapor boundary curve is a plot of the vapor pressure of the liquid (in this case, water) as a function of temperature. The liquid and its vapor are in equilibrium at each point on the curve. At each point on the solid–liquid boundary curve (for which the slope is slightly exaggerated), the solid and liquid are in equilibrium.

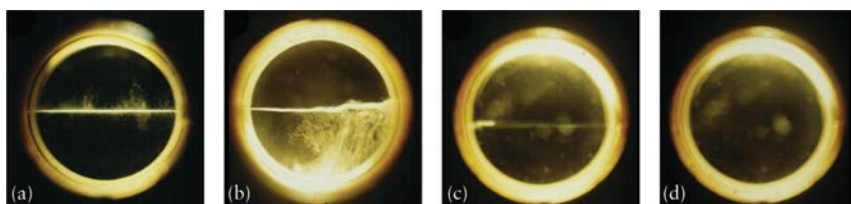
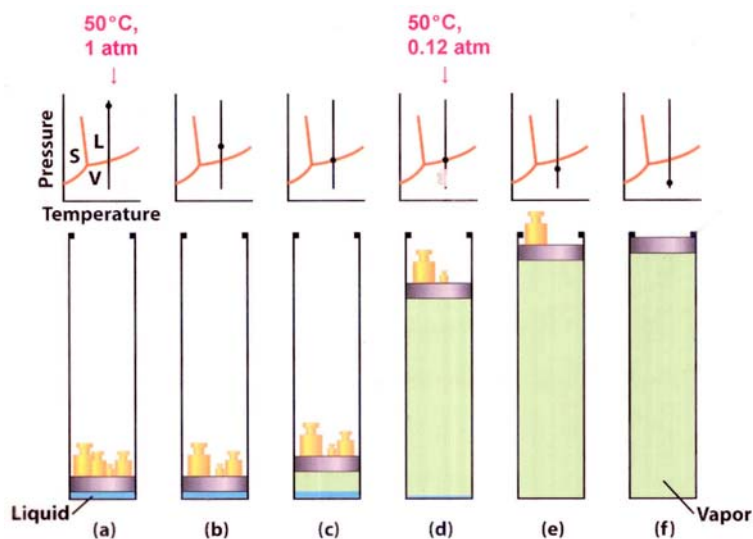


FIGURE 10.14 (a) At low temperatures the liquid and vapor phases of a substance in a sealed, constant-volume container are distinct. (b) As the temperature is raised, more of the liquid vaporizes; the density of the liquid decreases while the density of the vapor increases. (c) Near the critical temperature, T_c , the phases are less distinct, as they have nearly the same density. (d) At and above the critical temperature a single uniform phase, a supercritical fluid, fills the container.

Liquid and gas densities of water at temperatures and pressures near ambient conditions and at critical conditions:

At 1 atm and 0°C :

Density of Liquid H₂O = 1 g/mL = 55.6 mol/L

Density of Gaseous H₂O = 2.7×10^{-4} mol/L

At 218 atm and 374°C (critical conditions) :

Density of Liquid = Density of Gas = 4.1 mol/L

TABLE 10.4 Critical Temperatures and Pressures of Selected Substances

Substance	Critical temperature (°C)	Critical pressure (atm)
He	-268 (5.2 K)	2.3
Ne	-229	27
Ar	-123	48
Kr	-64	54
Xe	17	58
H ₂	-240	13
O ₂	-118	50
H ₂ O	374	218
N ₂	-147	34
NH ₃	132	111
CO ₂	31	73
CH ₄	-83	46
C ₆ H ₆	289	49

Effect of Temperature on Enthalpy of Vaporization

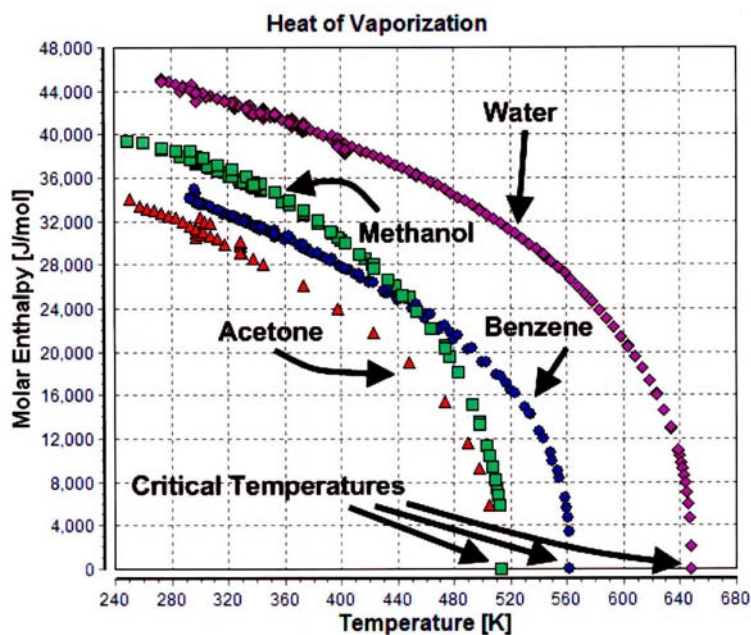


Table 14.1: Phase Properties of Selected Elements and Compounds**TABLE 14.1****Phase properties of selected elements and compounds^a**

	$\bar{C}_p(s)$ (cal/K mol)	$\rho(s)$ (g/cm ³)	T_f (K)	ΔH_{fus}° (kcal/mol)	$\bar{C}_p(l)$ (cal/K mol)	$\rho(l)$ (g/cm ³)	T_b (K)	ΔH_{vap}° (kcal/mol)	$\bar{C}_p(g)$ (cal/K mol)	T_3 (K)	P_3 (atm)	T_c (K)	P_c (atm)
He	...	0.198	3.9	0.147	4.2	0.02	5.0	2.2 ^b	0.050 ^b	5.2	2.24
Ne	6.5	1.43	24.6	0.08	8.7	1.25	27.1	0.43	5.0	24.6	0.43	44.4	27.2
Ar	8.4	1.62	83.8	0.27	10.7	1.40	87.3	1.61	5.0	83.8	0.68	150.9	48.3
Kr	8.6	2.79	115.8	0.38	11.1	2.44	119.9	2.17	5.0	115.8	0.72	209.4	54.3
Xe	8.5	3.39	161.4	0.52	11.0	2.97	165.1	3.02	5.0	161.4	0.81	289.7	57.6
H ₂	1.4	0.081	13.8	0.03	4.6	0.070	20.3	0.22	6.9	13.8	0.069	33.0	12.8
F ₂	17.3	1.3	53.5	0.12	13.7	1.108	85.0	1.62	7.5	53.5	0.0022	144.1	51.0
Cl ₂	13.4	1.9	172.2	1.53	15.6	1.367	238.6	4.86	8.1	172.	0.014	416.9	78.9
Br ₂	11.2	3.4	265.9	2.52	18.1	3.119	331.9	7.07	8.6	265.6	0.057	588.	102.0
I ₂	13.0	4.93	386.7	3.77	19.4	4.0	457.5	10.03	8.8	386.7	0.12	819.	...
HF	189.8	0.26	14.6	0.987	293.	6.19	7.0	189.	0.004	461.	63.9
HCl	12.1	...	159.0	0.33	14.4	1.187	188.	3.86	7.0	159.3	0.14	324.7	82.0
HBr	11.4	...	184.7	0.48	15.5	2.77	206.8	4.44	7.0	185.	0.29	363.2	84.4
HI	11.4	...	222.4	0.77	15.3	2.85	237.6	4.98	7.0	219.3	0.42	424.	82.0
O ₂	11.0	1.36	54.4	0.11	13.0	1.14	90.2	1.63	7.0	54.4	0.0015	154.6	49.8
O ₃	80.3	1.614	161.8	3.37	9.4	80.	6. × 10 ⁻⁶	261.1	55.0
S _(rhomb)	5.4	2.07	388.4	0.41	7.3	1.82	717.8	4.42	5.7	393.	0.0006	1314.	204.2
SO ₂	197.6	0.54	20.8	1.435	263.1	5.96	9.5	197.7	0.017	430.8	77.8
SO ₃	290.0	1.90	65.0	1.88	317.9	9.72	12.1	290.0	0.21
H ₂ O	9.0	0.917	273.15	1.436	18.0	1.000	373.15	9.716	8.6	273.16	0.0060	647.1	217.7
H ₂ S	187.6	5.22	16.2	0.96	213.6	4.67	8.2	185.3	0.19	373.2	88.2
H ₂ Se	207.4	2.12	231.9	4.71	411.	88.0
H ₂ Te	224.	1.67	...	2.57	271.	4.59
N ₂	11.0	1.027	63.2	0.17	13.8	0.804	77.4	1.33	7.0	63.2	0.125	126.2	33.5
P _(white)	5.7	2.69	317.3	0.16	...	1.745	550.	2.96	16.1	994.	...
N ₂ O	182.3	1.56	18.5	1.226	184.7	3.95	9.2	182.3	0.87	309.6	71.6
NO	8.7	...	109.5	0.55	15.0	1.269	121.4	3.31	8.9	109.0	0.20	180.	64.0