

Diagramas de fase

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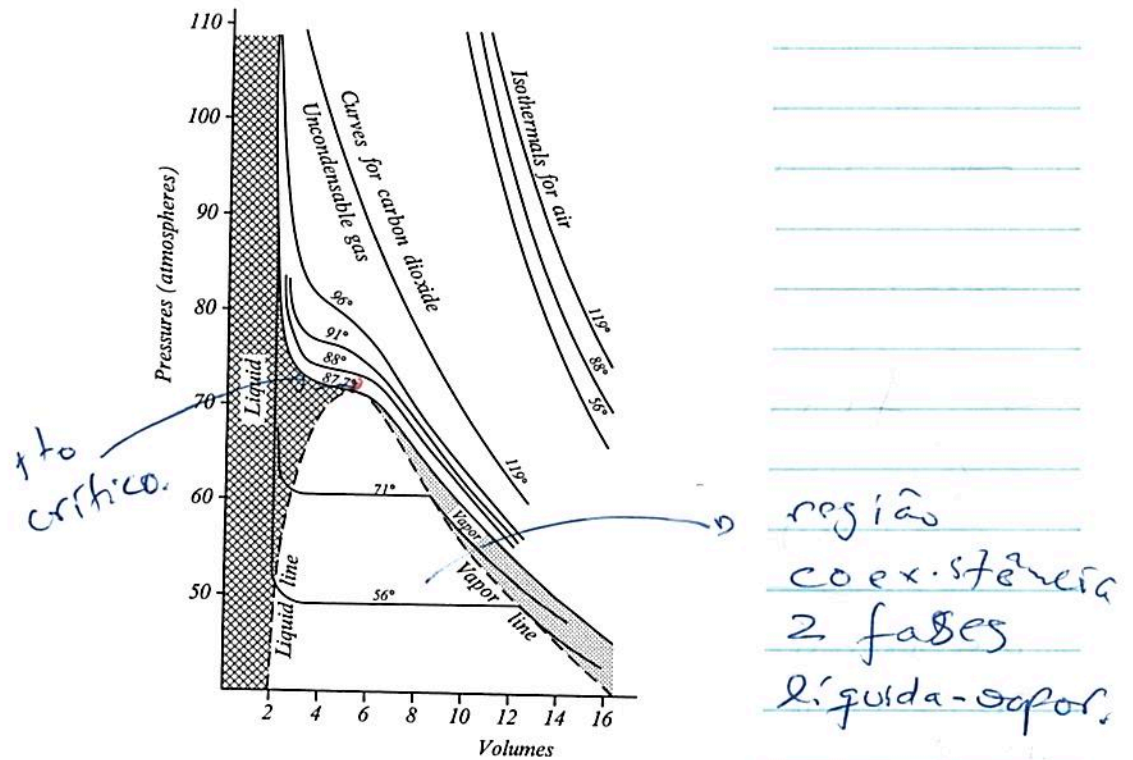


FIGURE 12.1 Phase diagram for carbon dioxide as measured by Thomas Andrews. Temperatures are in degrees Fahrenheit. Adapted from Mott-Smith, *The Concept of Heat*, p. 97.

87°F no temp crítica CO₂.

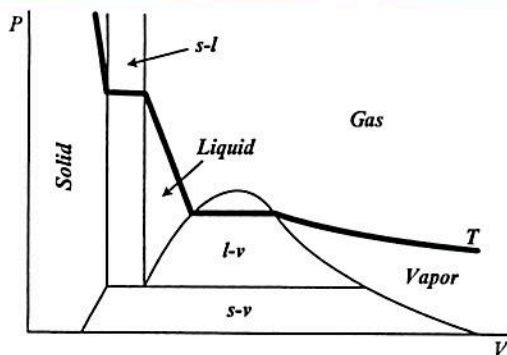


FIGURE 12.2 Isotherm (heavy line) in P-V space showing liquid-vapor and solid-liquid phase transitions. Solid-liquid (s-l), liquid-vapor (l-v), and solid-vapor (s-v) coexistence regions are indicated. Adapted from Walton, *Three Phases of Matter*, p. 12, Fig. 1.11c.

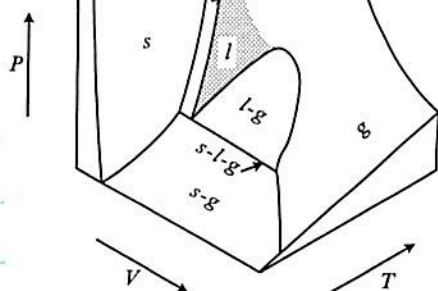
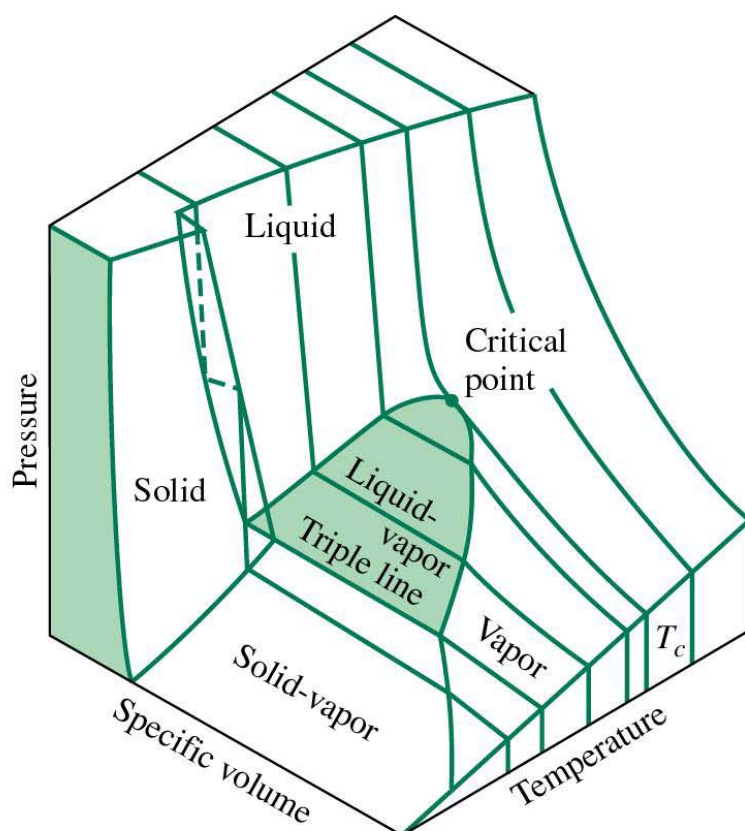
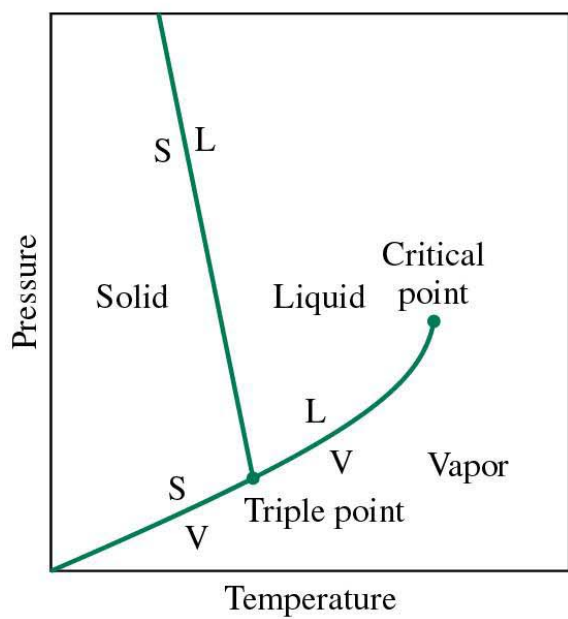


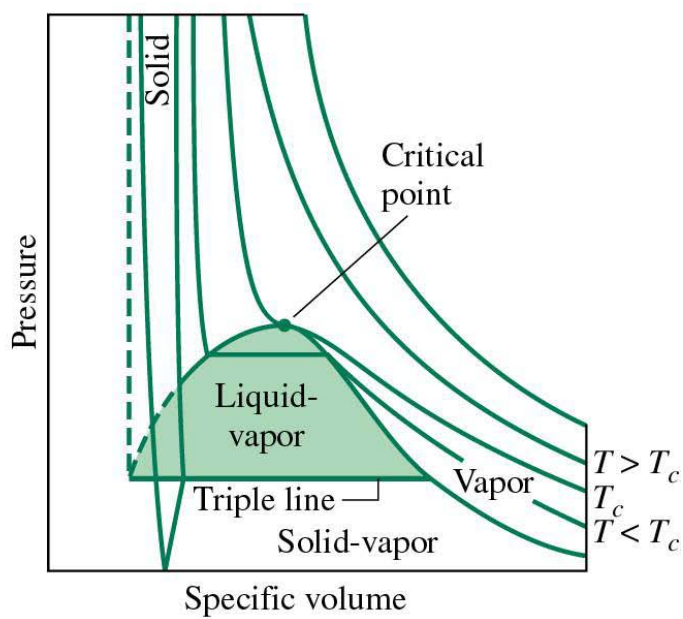
FIGURE 12.3 P-V-T surface of a substance that expands upon melting.



(a)



(b)



(c)

Um sistema que tenha mais de uma fase, pode ser dividido em 2 ^{ou mais} subsistemas para cada fase.

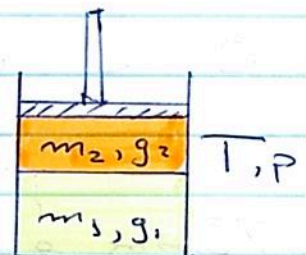
Somente reações químicas entre os constituintes ou transferência de massa entre as fases é que irão resultar alguma diferença do que já vimos até aqui.

Vamos considerar apenas a situação em que não hajam reações químicas.

↳ Equilíbrio entre fases

m_1 → parcela de massa na fase 1 (líquida)

m_2 → " " " " " 2 (vapor)



g_1 → ^{especifica.} fção Gibbs fase 1.
 g_2 → " " " 2.

$$G = m_1 g_1 + m_2 g_2, \quad G = G(p, T, m_1, m_2)$$

$$g_1 = g_1(p, T), \quad g_2 = g_2(p, T)$$

$$\text{a } p \text{ e } T \text{ ctes} \rightarrow dG = \frac{\partial G}{\partial m_1} dm_1 + \frac{\partial G}{\partial m_2} dm_2$$

$$\rightarrow \frac{\partial G}{\partial m_1} = g_1; \quad \frac{\partial G}{\partial m_2} = g_2, \quad \text{em equilíbrio a } dp=0 \text{ e } dT=0$$

$$\rightarrow dG = 0.$$

Obs: sistema total fechado 147

$$\rightarrow M = m_1 + m_2 \text{ é cte}$$

$$dM = dm_1 + dm_2 = 0 \rightarrow dm_1 = -dm_2$$

\therefore

$$dG = 0 \rightarrow (g_1 - g_2) dm_1 = 0$$

$$\hookrightarrow \boxed{g_1 = g_2} \text{ - eq. fase.}$$

\hookrightarrow obs 2: válido p/ caso geral c/ mais fases.

$$\rightarrow g_1 = g_2 = g_3 = \dots = g_n$$

E a volume cte e Temp. cte?

$$dV = 0 \quad dT = 0?$$

Tomos que a função apropriada é a energia livre de Helmholtz F

$$F = F(m_1, \vartheta_1, m_2, \vartheta_2, T); \quad \dots = V$$

$$\text{Mas } d(m_1 \vartheta_1 + m_2 \vartheta_2) =$$

$$\rightarrow m_1 d\vartheta_1 + m_2 d\vartheta_2 + \vartheta_1 dm_1 + \vartheta_2 dm_2 = 0 \quad (A)$$

$$\text{p/ equilíbrio } dF = 0 \rightarrow \text{com } F = m_1 f_1 + m_2 f_2$$

$$\rightarrow m_1 df_1 + m_2 df_2 + f_1 dm_1 + f_2 dm_2 = 0 \quad (B)$$

Multiplicando (A) por p e somando a (B)

$$(f_1 + p\vartheta_1) dm_1 + (f_2 + p\vartheta_2) dm_2 + m_1 (df_1 + p d\vartheta_1) + m_2 (df_2 + p d\vartheta_2) = 0$$

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$$df + Pd\sigma = 0$$

$$\rightarrow \therefore (f_1 + Pd\sigma_1)dm_1 + (f_2 + Pd\sigma_2)dm_2 = 0$$

$$\text{Como } M = m_1 + m_2 \rightarrow dm_1 = -dm_2$$

$$\rightarrow f_1 + Pd\sigma_1 = f_2 + Pd\sigma_2$$

$$\rightarrow \boxed{g_1 = g_2}$$

de fato esta condição é válida p/
restrições entre (dS, dV) , (dS, dp)
tabel.

\therefore Função de Gibbs tem relevân-
cia central na descrição de eq. entre
fases.

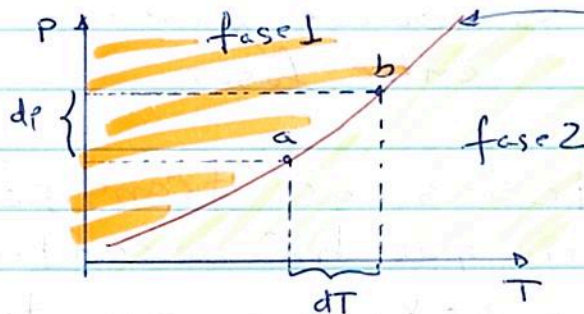
EQUAÇÃO DE CLAUSIUS-CLAPEYRON

pelo menos

Substância simples \rightarrow 2 graus de liberdade.
 $(p, V), (T, V), (p, T)$.

Mas se 2 fases (da subst.) coexistem em equilíbrio há um vínculo adicional.

Seja uma subst. simples c/ 2 fases:



Na fronteira entre as 2 fases:
 Como simas:
 $g_1^{(a)} = g_2^{(a)}$ e $g_1^{(b)} = g_2^{(b)}$

$$\rightarrow dg_1 = \left(\frac{\partial g_1}{\partial p} \right)_T dp + \left(\frac{\partial g_1}{\partial T} \right)_p dT$$

$$g_1(p, T), g_2(p, T)$$

$$= \sigma_1 dp - s_1 dT$$

$$G = U - TS + pV$$

e

$$g = u - Ts + p\sigma$$

$$dg_2 = \left(\frac{\partial g_2}{\partial p} \right)_T dp + \left(\frac{\partial g_2}{\partial T} \right)_p dT$$

$$dg = \sigma dp - s dT$$

$$= \sigma_2 dp - s_2 dT$$

- Como $g_1 = g_2$ na fronteira de coexistência:

$$dg_1 = dg_2 \rightarrow \sigma_1 dp - s_1 dT = \sigma_2 dp - s_2 dT$$

$$\hookrightarrow (\sigma_1 - \sigma_2) dp = (s_1 - s_2) dT \rightarrow \frac{dp}{dT} = \frac{(s_1 - s_2)}{(\sigma_1 - \sigma_2)}$$

Com $\Delta S = \frac{Q}{T}$ $\rightarrow \frac{dp}{dT} = \frac{\Delta S}{\Delta V}$

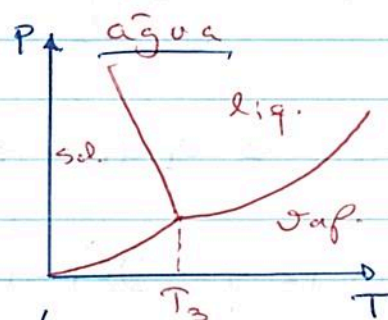
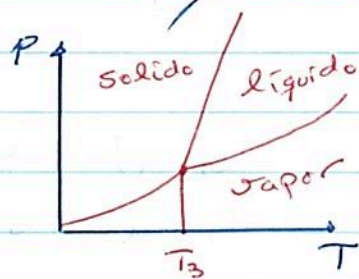
$\sigma_1 - \sigma_2 = \Delta \sigma$

proc. rev. $\rightarrow \Delta S = \frac{Q}{T} \rightarrow Q = L \equiv \text{calor latente.}$

$\rightarrow \frac{dp}{dT} = \frac{L}{T \Delta V}$ eq. Clausius-Clapeyron.

\hookrightarrow descreve fronteira entre fases.

\hookrightarrow descreve todas as transições de fase em que há descontinuidade na entropia e volume na transição, (Transições de fase de 1ª ordem.)



$T_3 \rightarrow g_s = g_l = g_v$

\hookrightarrow sol. aumenta
liq. \rightarrow sol.

Se a pressão não for muito alta.
ou próxima ao pto crítico.

vapor \sim gás ideal

$$\rightarrow \frac{dp}{dT} = \frac{1}{T \Delta V} = \frac{\alpha p}{T^2 R}, \quad \alpha \equiv \text{calor latente molar.}$$

α ?

$$(a) \quad \alpha \text{ é cte} \quad \rightarrow \cdot \frac{dp}{p} = \frac{\alpha}{R} \frac{dT}{T^2} \rightarrow R \ln p = -\frac{\alpha}{T} + C$$

$$\rightarrow p = p_0 e^{-\alpha/RT}$$

(b) Se capacidades caloríficas nas 2 fases
forem constantes:

$$\text{Como } \alpha = T(S_v - S_c), \quad v = \text{vapor} \\ c = \text{condensado}$$

$\frac{d}{dT}$ ao longo da fronteira de fase:

$$\frac{d}{dT} \left(\frac{\alpha}{T} \right) = \frac{dp}{dT} \frac{\partial}{\partial p} \left(\frac{\alpha}{T} \right)$$

$$\rightarrow \frac{d}{dT} \left(\frac{\alpha}{T} \right) = \frac{\partial}{\partial T} (S_v - S_c) + \frac{dp}{dT} \frac{\partial}{\partial p} (S_v - S_c) \\ = \frac{C_{pv} - C_{pc}}{T} + \frac{dp}{dT} \left[\frac{\partial S_v}{\partial p} - \frac{\partial S_c}{\partial p} \right]$$

pelos rel. Maxwell:

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$$\frac{d}{dT} \left(\frac{L}{T} \right) = \frac{C_{pV} - C_{pC}}{T} - \left[\frac{\partial(V_V - V_C)}{\partial T} \right]_P \frac{dp}{dT}$$

Se $V_V \gg V_C$ supomos novamente vapor como gás ideal

$$\sim \frac{dp}{dT} = \frac{L_P}{RT^2} \quad \left(\frac{\partial V_V}{\partial T} \right)_P = \frac{nR}{P}$$

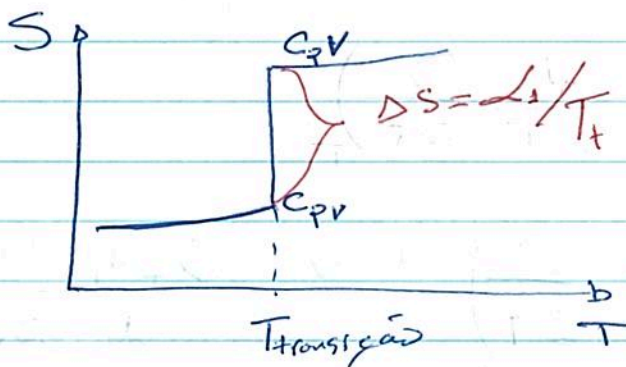
$$\rightarrow \frac{d}{dT} \left(\frac{L}{T} \right) = \frac{C_{pV} - C_{pC}}{T} - \frac{L}{T^2}$$

$$\text{ou } dL = (C_{pV} - C_{pC}) dT$$

$$C_p L = L_0 + L_1 T$$

$$p / \frac{dp}{dT} = \frac{L_P}{RT^2} \rightarrow R \ln p = -\frac{L_0}{T} + L_1 \ln T + \frac{L_2}{T^2}$$

$$L_1 = C_{pV} - C_{pC}$$



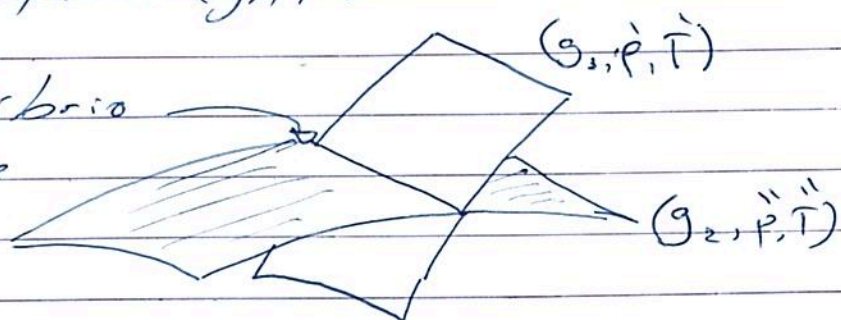
$\Delta S \xrightarrow{0}$ mudança de estado
mais ordenado
p/ menos ordenado.

Calor latente
Em energia fornecida p/
mudança de ordem.

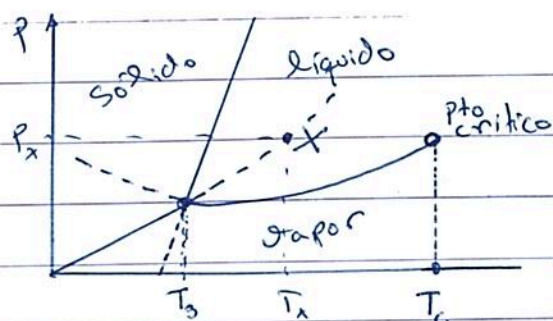
Função de Gibbs e Transições de 1ª Ordem

Fase: superfície em plano (g, p, T)

2 fases coexistentes: ^{linha} equilíbrio de fase



3. fases: sólido, líquido, vapor:



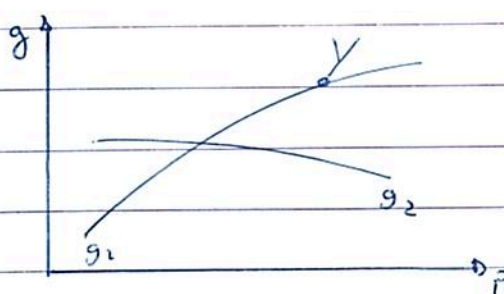
----- fronteira entre fases.
menos estável que
região em que está
inserida.

X é interseção entre sólido
e vapor

mas não é estável pois p/p_x e T_a
a superfície p/g líquida é
mais estável. (menor valor).

- seção p/T constante:

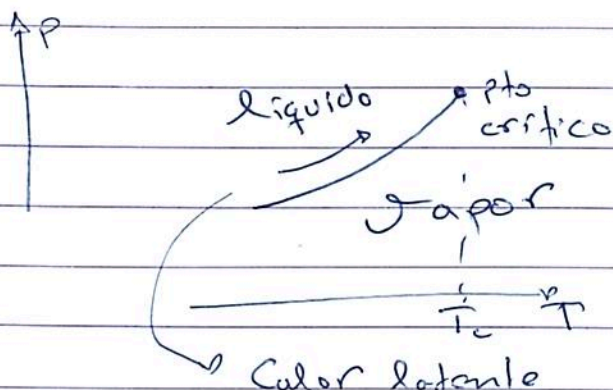
p um dado $\{p$ e $T\}$
o estado mais estável é o
em que g é menor
 $\therefore Y$ é meta estável.



Estados metaestáveis p vapor supersaturado.

líquido superaquecido

líquido super-resfriado.

Pto crítico

$$dg = \left(\frac{\partial g}{\partial p} \right)_T dp + \left(\frac{\partial g}{\partial T} \right)_p dT$$

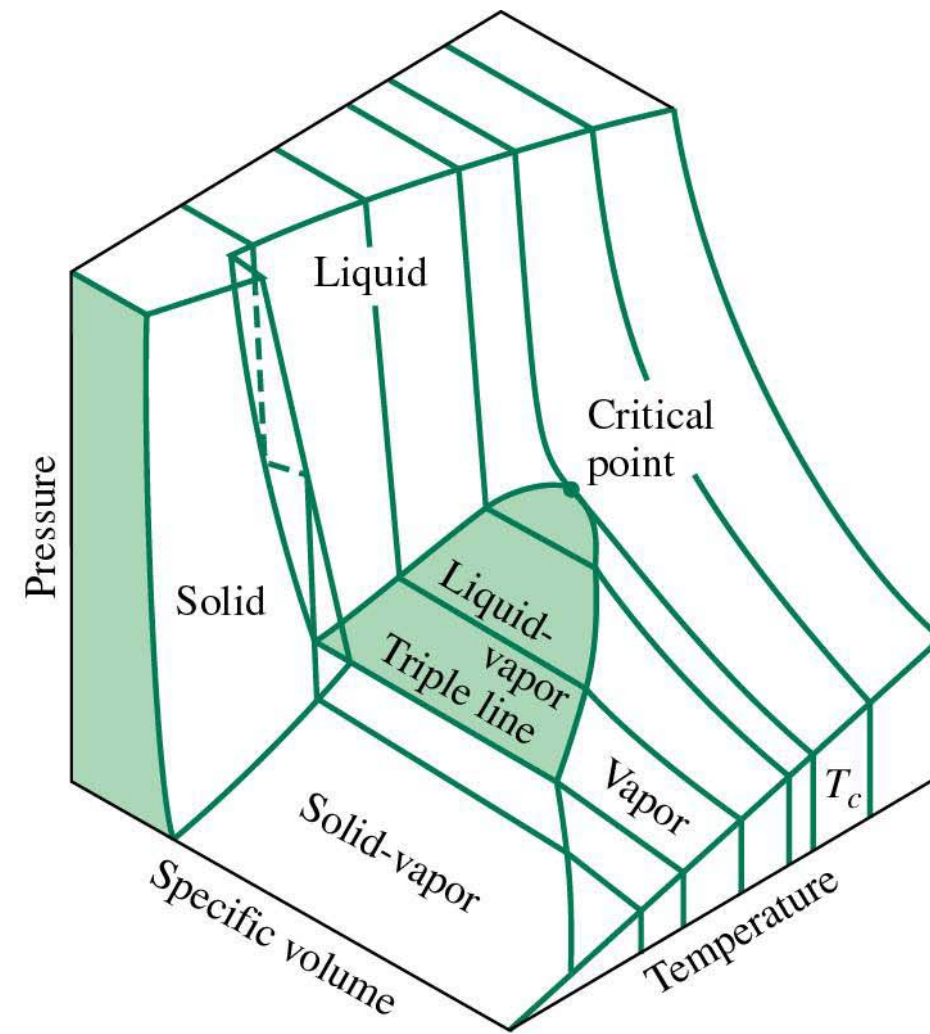
$$= v dp - s dT$$

Na transição
líquido - vapor.

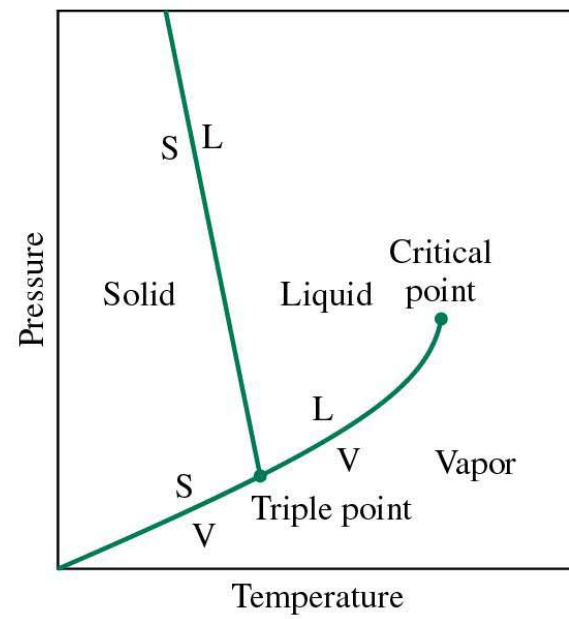
e mudança no volume diminuem até
não existirem p/ pto crítico.

p/ $T > T_c$ é possível se passar
continuamente entre as fases.

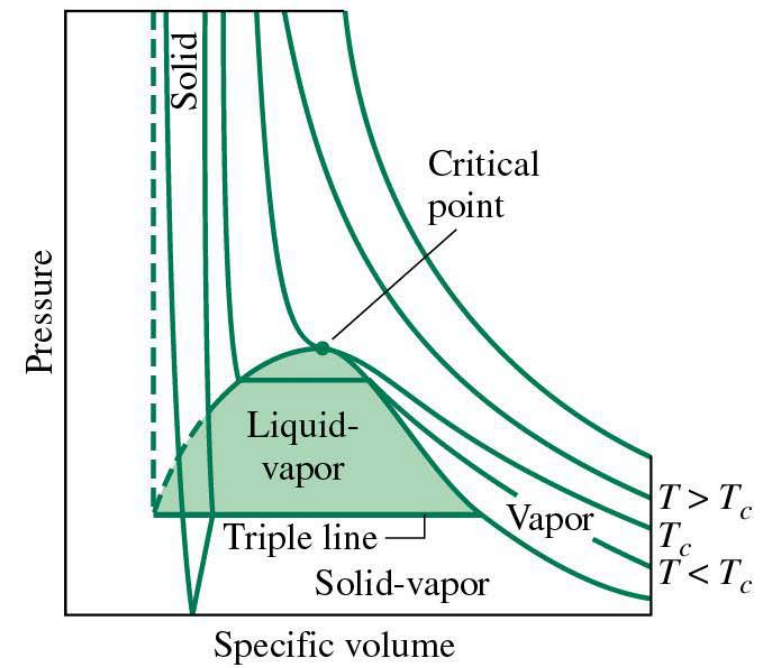
$$T \Delta s = - T \Delta \left(\frac{\partial g}{\partial T} \right)_p ; \quad \Delta v = \Delta \left(\frac{\partial g}{\partial p} \right)_T$$



(a)

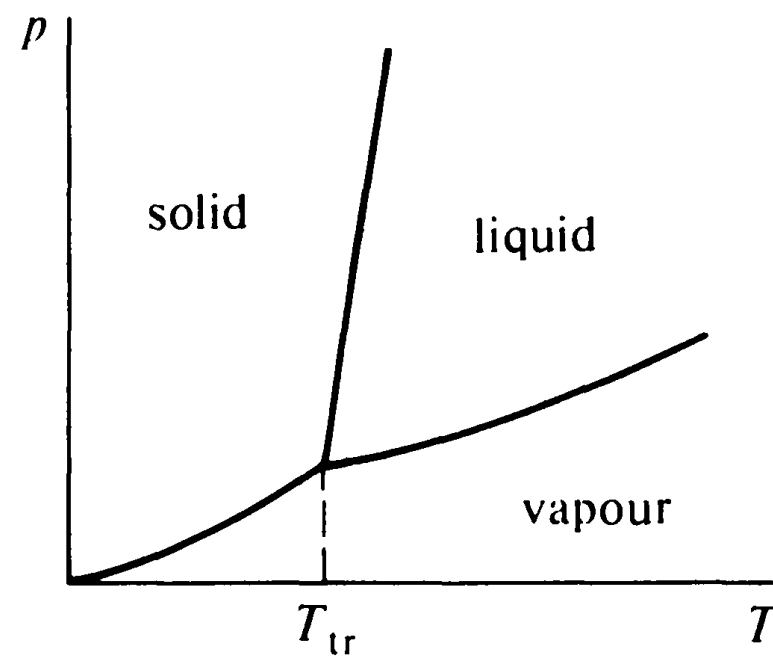


(b)

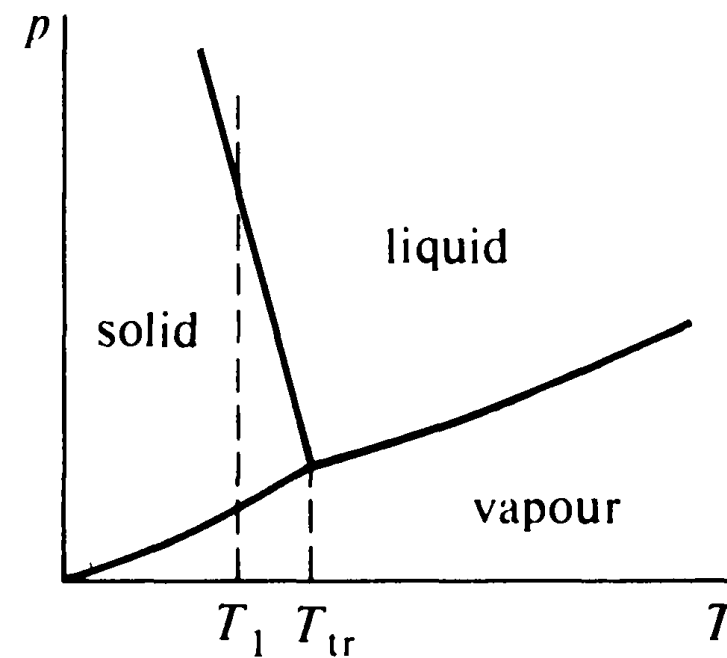


(c)

Fig. 10.3. Phase diagrams. (a) is typical of most simple substances, while (b) shows the behaviour of water which expands on freezing.



(a)



(b)

Fig. 10.4. A phase diagram as the projection of the intersections of the g surfaces of the component phases.

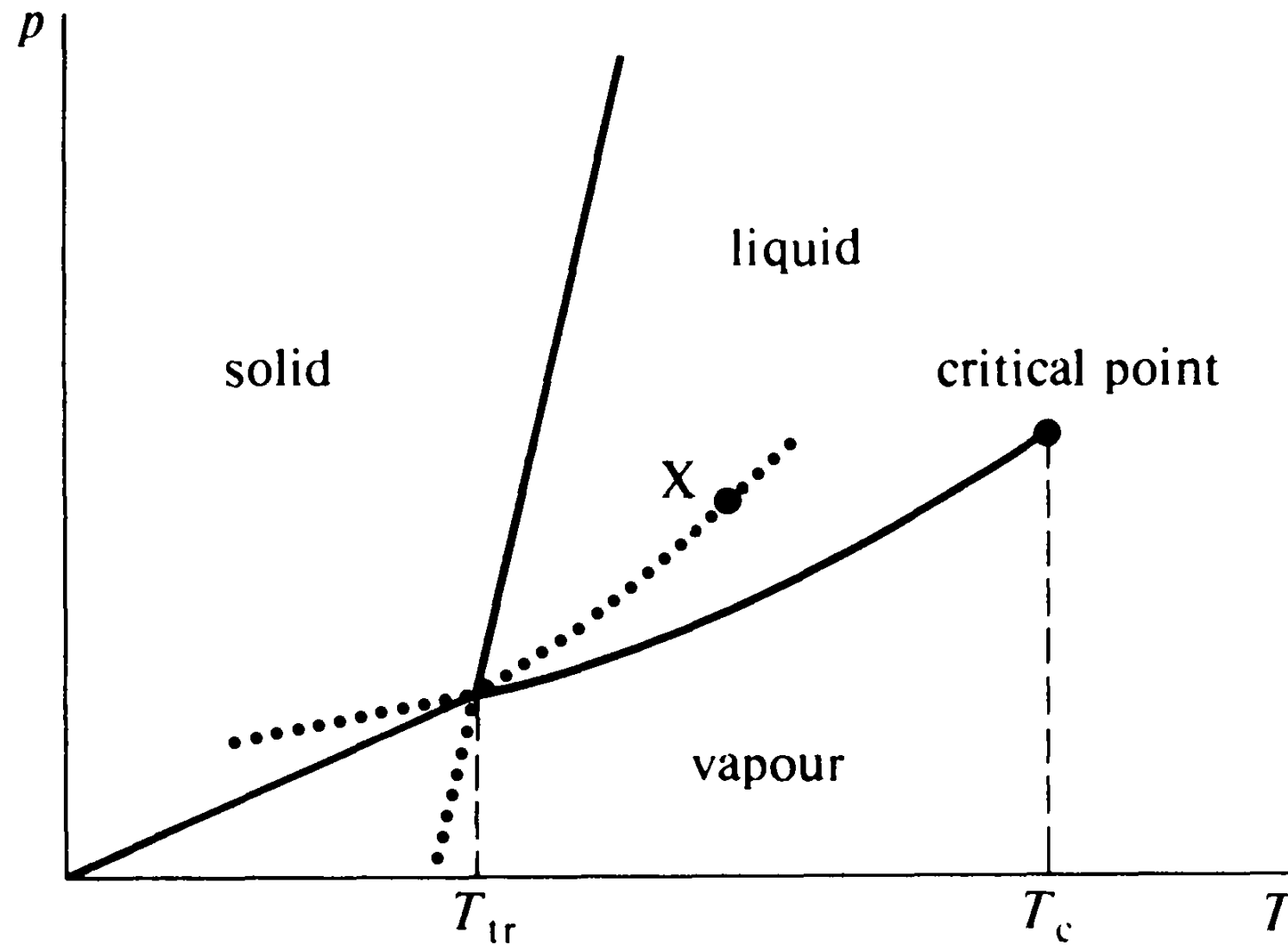


Fig. 10.5. A section through the g surfaces in a plane of constant temperature.

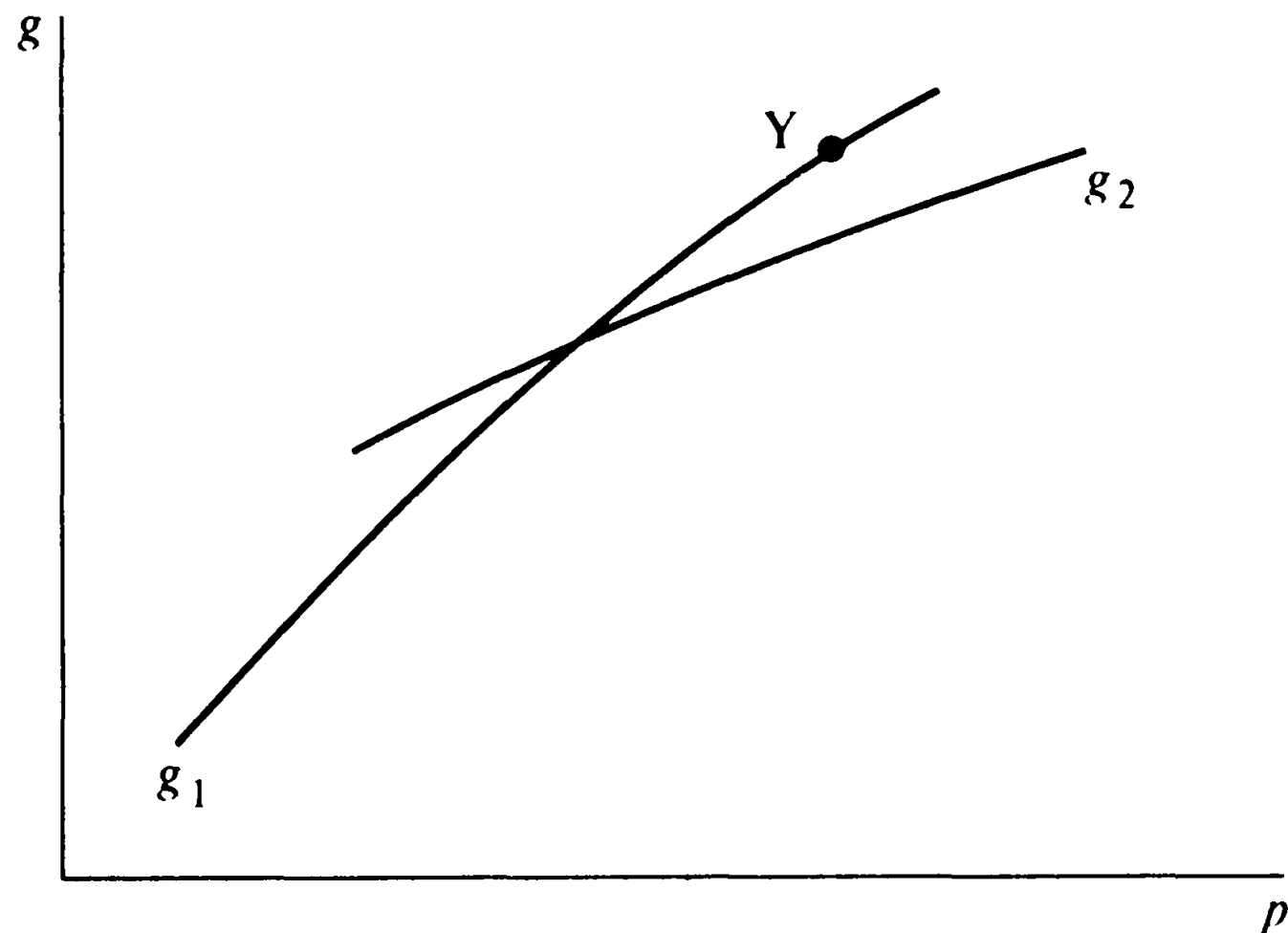


Fig. 10.7. Van der Waals isotherms near the critical temperature (not to scale).

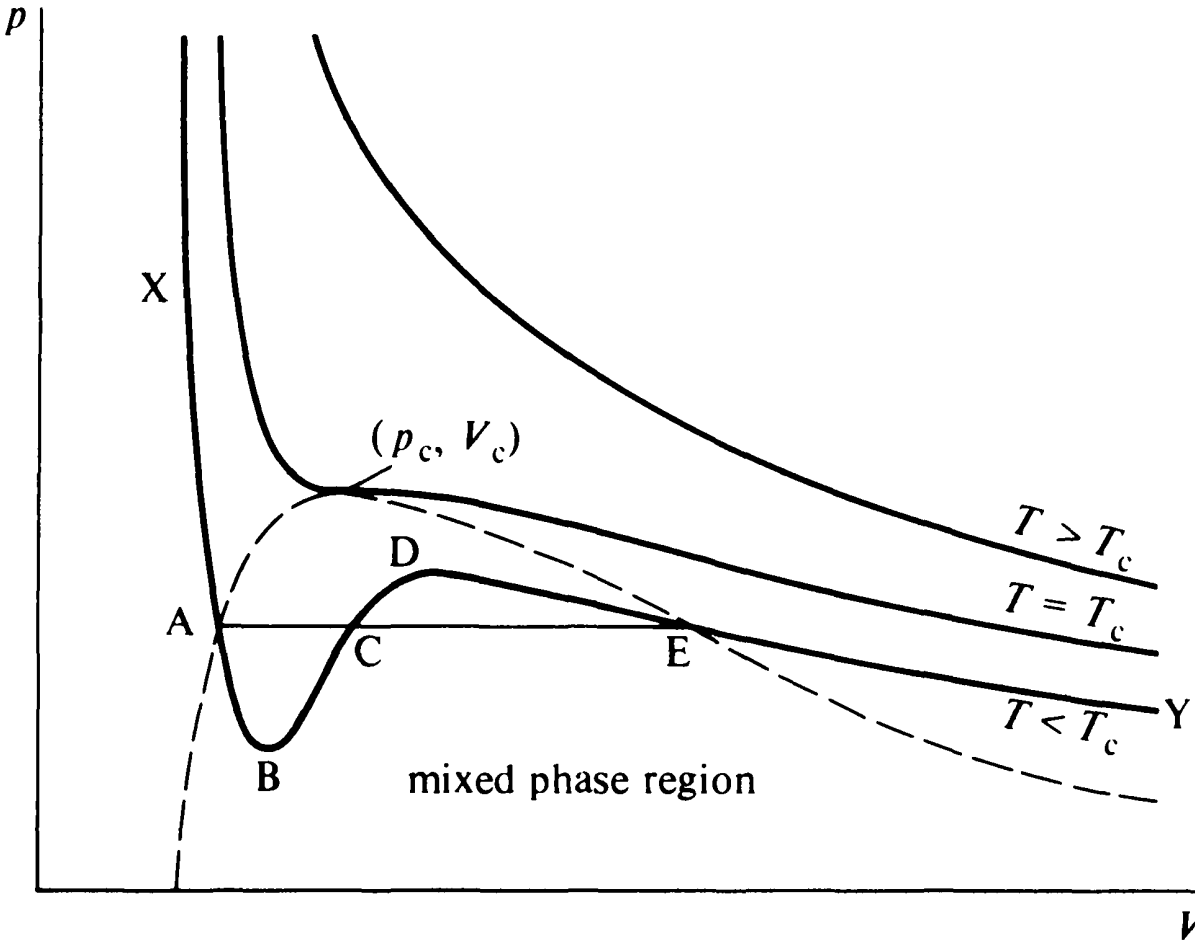


Fig. 10.8. The Gibbs function of a van der Waals fluid below the critical temperature.

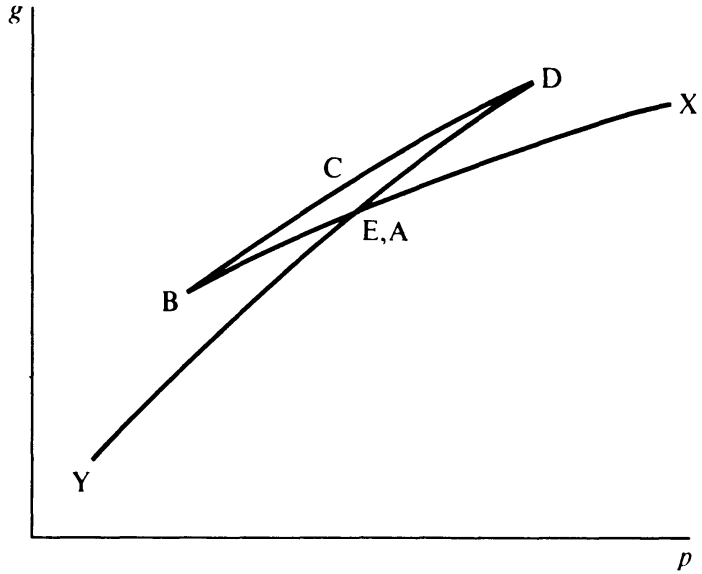


Fig. 10.9. The Gibbs function of a van der Waals fluid near the critical point.

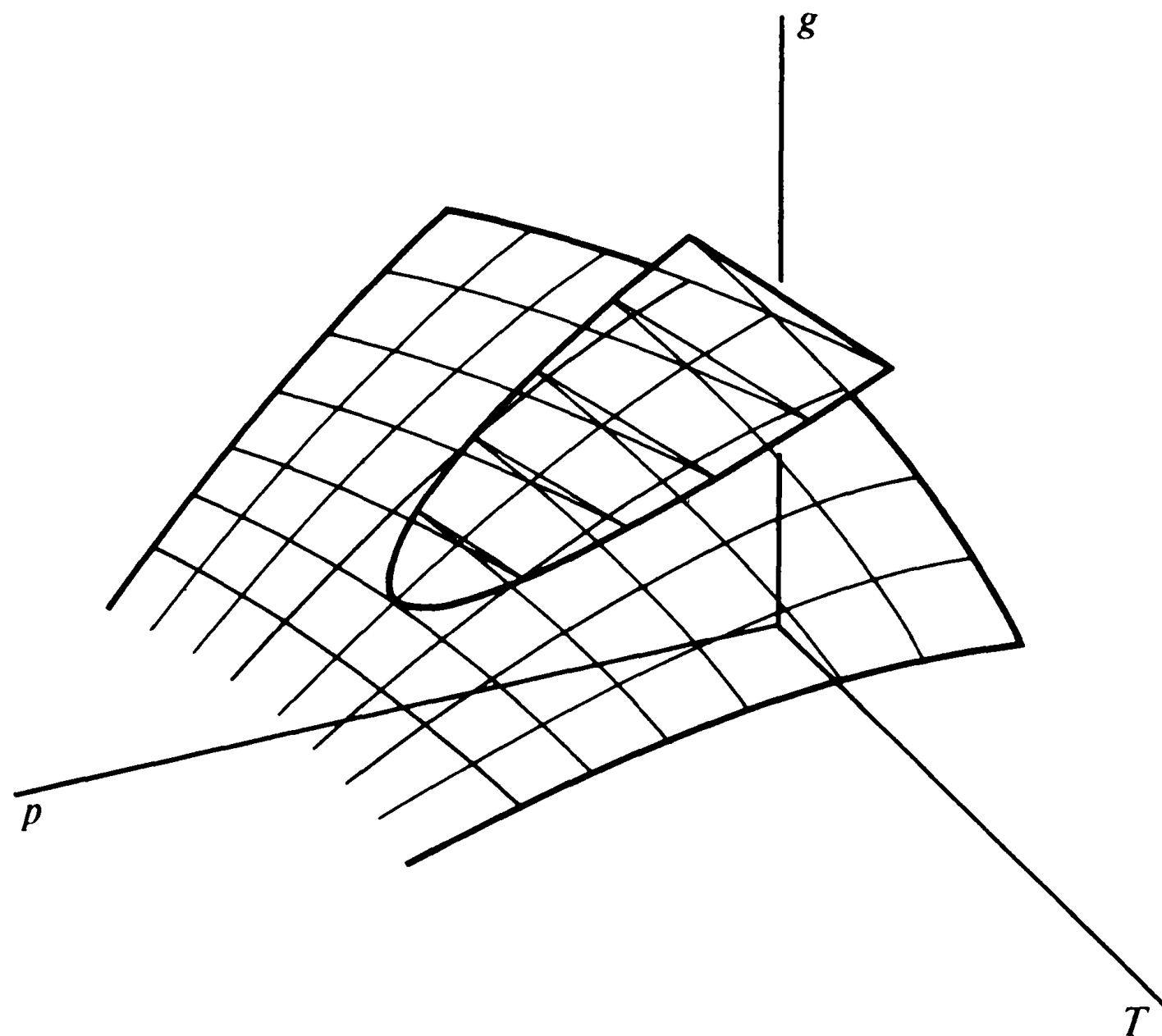


Table 10.1. *First, second, and third order transitions*

The table lists, for each order of transition, the differential coefficients of g and the most closely related experimental quantities in which discontinuity appears.

Order	Discontinuity appears in:				
	Differentials of g		Corresponding experimental quantities		
First	s	v	s	v	
Second	$\left(\frac{\partial s}{\partial T}\right)_p$	$\left(\frac{\partial v}{\partial T}\right)_p$			
			c_p	β	κ
	$\left(\frac{\partial s}{\partial p}\right)_T$	$\left(\frac{\partial v}{\partial p}\right)_T$			
Third	$\left(\frac{\partial^2 s}{\partial T^2}\right)_p$	$\left(\frac{\partial^2 v}{\partial T^2}\right)_p$			
			$\left(\frac{\partial c_p}{\partial T}\right)_p$	$\left(\frac{\partial \beta}{\partial T}\right)_p$	$\left(\frac{\partial \kappa}{\partial T}\right)_p$
	$\frac{\partial^2 s}{\partial p \partial T}$	$\frac{\partial^2 v}{\partial p \partial T}$			
			$\left(\frac{\partial c_p}{\partial p}\right)_T$	$\left(\frac{\partial \beta}{\partial p}\right)_T$	$\left(\frac{\partial \kappa}{\partial p}\right)_T$
	$\left(\frac{\partial^2 s}{\partial p^2}\right)_T$	$\left(\frac{\partial^2 v}{\partial p^2}\right)_T$			

Fig. 10.10. The behaviour of the Gibbs function and its first two derivatives in first and second order transitions.

