Spring 2001

Thermodynamics
Solutions
Assignment #6

9.3-1 From clapeyron equation $\frac{dP}{dT} = \frac{\ell}{T\Delta v}$

we obtain $\Delta T = \frac{T \Delta v}{\ell} \Delta p$

Let $\Delta v = v_g - v_\ell \simeq v_g = \frac{RT}{P}$

Then $\Delta T = \frac{RT^2}{\ell} \frac{\Delta P}{P}$

$= 3.98$

Liquid boils at $\underline{\underline{131\ ^\circ C}}$

but $\Delta p = 10$ mm Hg
$P = 800$ mm Hg
$\ell = 1000$ cal/mole
$R = 1.99$ cal/mole-kelvin
$T = 127 + 273 = 400$

9.3-3 From Clapeyron equation and the assumption $v_g >> v_\ell$

we obtain $\frac{dP}{dT} \simeq \frac{\ell P}{RT^2}$

Let $P = P_0 e^{-mgh/RT}$ where P_0 = pressure when $h = 0$

Assume $mgh/RT << 1$, then

$P = P_0 \left(1 - \frac{mgh}{RT}\right)$ and $dP = -P_0 \left(\frac{mg}{RT}\right) dh$

Thus $\frac{dh}{dT} = -\frac{\ell}{mgT}$

$= 39.5$

$dh = 39.5\ dT$

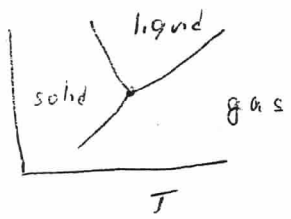
$= \underline{\underline{395 \text{ meters}}}$

$\ell = 1000$ cal/mole $= 4186$ J/mole
$g = 9.8$
$m = 29 \frac{g}{mole} = 0.029 \frac{kg}{mole}$ = gm mol. wt. of air
$T \simeq 373$ K

verify $\frac{mgh}{RT} << 1$ $\quad \frac{mgh}{RT} = 3.6 \times 10^{-2} << 1$

9.3-5 liquid-gas $\ln P = 24.38 - \frac{3063}{T}$

solid-gas $\ln P = 27.92 - \frac{3754}{T}$



At the triple point

$$P_{liquid} = P_{solid} = P_{gas}$$

$$T_{liquid} = T_{solid} = T_{gas}$$

Solving simultaneously the two equations yields the co-ordinate of the triple point: $T_{tp} = 195\ K$ $P_{tp} = 5800\ Pa$

From Clapeyron equation and the assumption $v_g >> v_l$ and $v_g >> v_s$

$$\frac{dP}{dT} = \frac{\ell P}{RT^2}$$

or

$$\frac{dP}{P} = \frac{\ell}{R}\frac{dT}{T^2}$$

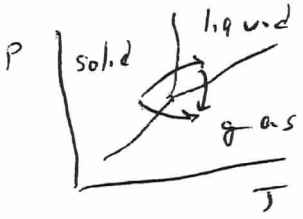
Integrating

$$\ln P = \text{constant} - \frac{\ell}{RT}$$

Thus $\ell_{liquid-gas} = \ell_{vaporization} = 3063 \times R = 25.47 \times 10^3 \frac{J}{mole}$

and $\ell_{solid-gas} = \ell_{sublimation} = 3754 \times R = 31.21 \times 10^3 \frac{J}{mole}$

Since the internal energy of a substance is a function of the state, not its past history in the vicinity of the triple point



$$\ell_{fusion} + \ell_{vaporization} = \ell_{sublimation}$$

or

$$\ell_{fusion} = \ell_{sublimation} - \ell_{vaporization}$$

$$= 5.74 \times 10^3 \frac{J}{mole}$$

9.3-7 Along the co-existance curve

$$\frac{dP}{dT} = \frac{\ell}{T\Delta v} \qquad \text{where } \Delta v \simeq v_g \simeq \frac{RT}{P}$$

$$= \frac{\ell P}{RT^2}$$

$$\frac{dP}{P} = \frac{dT}{T^2}\frac{\ell}{R} \qquad \text{integrating}$$

$$\ln \frac{P_f}{P_i} = \frac{\ell}{R}\left(\frac{1}{T_i} - \frac{1}{T_f}\right)$$

$P_i = 1\times10^5$ Pa $\quad P_f = 2\times10^5$ Pa $\quad \ell = 5\times10^3 \frac{J}{mole}$ $\quad T_i = 300$ K

$v_{gi} = 10^{-2}$ m^3 $\quad N_g + N_\ell = 1$ $\quad V_{total} = 10^{-2}$ m^3

$$\text{Initial mole fraction} = X_i = \frac{N_{gi}}{N_{gi}+N_{\ell i}} = N_{gi}$$

$$N_{gi} = \frac{PV}{RT} = \frac{1\times10^5\times10^{-2}}{8.3\times300} = 0.4$$

$$\therefore \boxed{X_i = 0.4}$$

$$\frac{1}{T_f} = \frac{1}{T_i} - \frac{R}{\ell}\ln\frac{P_f}{P_i} = \frac{1}{300} - \frac{8.3}{5\times10^3}\ln 2$$

$$T_f = 458\,K$$

and $X_f = \frac{2\times10^5\times10^{-2}}{8.3\times458} = 0.53$ //

9.4-3 From the equations on page 241 of Callen

$$T_{cr} = \frac{8a}{R\times27b} = \underline{\underline{636\ K}}$$

$a = 0.544$

$b = 30.5\times10^{-6}$

$$P_{cr} = \frac{a}{27b^2} = \underline{\underline{2.16\times10^7\ Pa}}$$

Observed value of critical temperature is 647 K. Agreement is reasonable but not spectacular. Note the comment on page 242 of Callen "a and b are obtained by empirical curve fitting to the van der Waals isotherms in the vicinity of 273 K; they ... less satisfactorily."