**10.40 Thermodynamics** **Fall 2003**
**Exam 1**

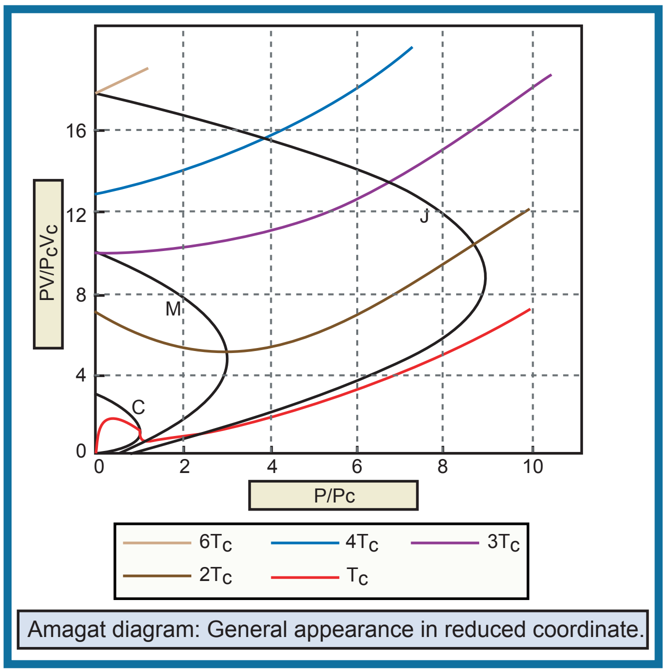
Problem 3

3. (30 points) A French Physicist, Emile Amagat ( 1841-1915) developed a diagram of *PV versus P* to represent important volumetric behavior for a single component system. Amagat claims that his diagram, illustrated below in reduced coordinates for a general pure substance, provides the same information content as the *P versus V* diagram we have discussed frequently in class, but that it allows for improved visualization of behavior at low and high pressures or densities. On the Amagat diagram three parabolic curves (C, M, and J) are shown along with a number of isotherms at multiple values of $T_c$. The outer curve J is the locus of Joule-Thompson coefficient inversion temperatures where the partial derivative of $T$ as a function of $P$ at constant $H$ changes sign.

(a) (10 points) The intermediate curve M is the locus of *PV* product minima as a function of *P*. Show that the intercept of this locus with the reduced *PV* axis at $P_r = 0$ corresponds to the reduced Boyle temperature of the fluid.

(b) (10 points) At high pressures the isotherms become nearly parallel. Develop an analysis based on the VdW EOS that shows this to be reasonable and estimate the limiting value of *PV/P* as $P \rightarrow \infty$ .

(c) (10 points) The inner curve C is the locus of points representing liquid and vapor phase co-existence or the binodal curves meeting at the critical point with a vertical tangent. Is this behavior consistent with the stability criteria described in chapter 7 of the text? Specifically show that the criteria given by Equations (7-16 and 7-39) are satisfied at the critical point. Explain your answer.




Amagat diagram: General appearance in reduced coordinate.

Image by MIT OCW.

**Solution**

(a)

The definition of the Boyle Temperature is given on p. 249, text as,

$$\left(\frac{\partial Z}{\partial P}\right)_{T=T_{Boyle}} = 0 \qquad \text{as } P_r \to 0$$

Since M is a locus of minima, for every point on curve M: $\left(\frac{\partial \left(P_r V_r\right)}{\partial P_r}\right)_T = 0$

$$\left(\frac{\partial \left(P_r V_r\right)}{\partial P_r}\right)_T = RTV_c\left(\frac{\partial Z}{\partial P}\right)_T$$

$$\left(\frac{\partial \left(PV\right)}{\partial P}\right)_T = 0 = RTV_c\left(\frac{\partial Z}{\partial P}\right)_T$$

Since $R$, $T$, and $V_c \neq 0$, $\left(\frac{\partial Z}{\partial P}\right)_T$ =0

At $P_r = 0,\ T = T_{Boyle}$ for $\left(\frac{\partial \left(P_r V_r\right)}{\partial P_r}\right)_T$ by the definition of the Boyle temperature.

Thus, the intercept of curve M with the reduced PV axis at $P_r$ corresponds to the Boyle temperature of the fluid.

(b)

van der Waals equation of state: $$P = \underbrace{\frac{RT}{V-b}}_{\text{repulsive term}} - \underbrace{\frac{a}{V^2}}_{\text{attractive term}} \qquad (1)$$

As $P \to \infty$, repulsive forces dominate (i.e. b, the exclusion volume, is a positive, finite number, so that $V \to b$ before $V \to 0$),

$$\frac{RT}{V-b} \gg \frac{a}{V^2}$$

The vdW EOS reduces to

$$P = \frac{RT}{V-b} \qquad (2)$$

At high pressures, the isotherms all have the same slope. Since the isotherms form straight lines at high pressures, they have a constant slope. To show that the high pressure isotherms have the same slope (i.e. are parallel), we evaluate the derivative, $\left(\frac{\partial(PV)}{\partial P}\right)_T$.

Using the chain rule,

$$\left(\frac{\partial(PV)}{\partial P}\right)_T = P\left(\frac{\partial V}{\partial P}\right)_T + V$$

From equation (2), $\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{(V-b)^2}$

Thus,

$$\left(\frac{\partial(PV)}{\partial P}\right)_T = \left(\frac{\cancel{RT}}{\cancel{(V-b)}}\right)\left(\frac{(V-b)^{\cancel{2}}}{-\cancel{RT}}\right) + V = -V + b + V$$

$$\left(\frac{\partial(PV)}{\partial P}\right)_T = b$$

So at high pressure, all isotherm slopes tend to the same value, b.

Also, as $P \to \infty$,

$$\lim_{P\to\infty}\left(\frac{\cancel{P}V}{\cancel{P}}\right) = \lim_{P\to\infty}(V) = b$$

since the denomiator of $P = \frac{RT}{V-b}$ must go to zero as $P \to \infty$.

(c)

Where curve C and the critical temperature isotherm meet is the critical point. The slope of the lines at the critical point is vertical. The critical point is also an inflection point.

First, we show that equation (7-16) is satisfied at the critical point by using the first derivative of PV in terms of P.

$y^{(m-2)}_{(m-1)(m-1)} = 0$ with $m = n+2 = 3$ for pure component case

$$y^{1}_{22} = A_{VV} = -\left(\frac{\partial P}{\partial V}\right)_T = 0 \qquad (7\text{-}16)$$

$$\left(\frac{\partial(PV)}{\partial P}\right)_{T=T_C} = \infty \quad \text{at the critical point} \qquad (3)$$

Show that equation (3) is satisfied by using equation (7-16).

$$\left(\frac{\partial(PV)}{\partial P}\right)_{T=T_C} = V + P\underbrace{\left(\frac{\partial V}{\partial P}\right)_{T=T_C}}_{\frac{1}{A_{VV}}=\frac{1}{0}\rightarrow\infty} \qquad \text{by equation (7-16)}$$

$$\left(\frac{\partial(PV)}{\partial P}\right)_{T=T_C} = \infty$$

The above equation agrees with equation (3). Thus, the criterion given in equation (7-16) is satisfied at the critical point.

Now, we examine the second derivative to determine if its behavior is consistent with equation (7-39).

$$y^{(m-2)}_{(m-1)(m-1)(m-1)} = 0 \quad \text{with } m = n+2 = 3 \text{ for pure component case}$$

$$y^{1}_{222} = A_{VVV} = -\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \tag{7-39}$$

By switching the axis on the Amagat diagram so that PV is the dependent axis and P is the independent axis, we can see that the critical point is also an inflection point, so

$$\left(\frac{\partial^2 P}{\partial(PV)^2}\right)_{T=T_C} = 0 \quad \text{at the critical point} \tag{4}$$

Let $x \equiv \left(\frac{\partial P}{\partial(PV)}\right)_{T=T_C} = \frac{1}{V + P\left(\frac{\partial V}{\partial P}\right)_{T=T_C}}$

$$\left(\frac{\partial^2 P}{\partial(PV)^2}\right)_{T=T_C} = \left(\frac{\partial(x)}{\partial(PV)}\right)_{T=T_C} = \left[\left(\frac{\partial(x)}{\partial(PV)}\right)_{T=T_C}\right]^{-1} = 0 \tag{5}$$

$$\left(\frac{\partial^2 P}{\partial(PV)^2}\right)_{T=T_C} = \left[V\left(\frac{\partial P}{\partial x}\right)_T + P\left(\frac{\partial V}{\partial x}\right)_T\right]^{-1} = 0 \tag{6}$$

Therefore, either $\left(\frac{\partial P}{\partial x}\right)_T$ and/or $\left(\frac{\partial V}{\partial x}\right)_T = 0$.

$$\left(\frac{\partial P}{\partial x}\right)_T = \left(\frac{\partial x}{\partial P}\right)_T^{-1} = \left[\frac{\partial}{\partial P}\left(\frac{1}{V + P\left(\frac{\partial V}{\partial P}\right)_T}\right)\right]^{-1}$$

We want derivatives that look like $\left(\frac{\partial P}{\partial V}\right)_T$ and $\left(\frac{\partial^2 P}{\partial V^2}\right)_T$ because we have relations for them given in equations (7-16) and (7-39).

Multiply the denominator and numerator by $\left(\frac{\partial P}{\partial V}\right)_T$ to yield,

$$\left(\frac{\partial P}{\partial x}\right)_T = \left[\frac{\partial}{\partial P}\left(\frac{\left(\frac{\partial P}{\partial V}\right)_T}{V\left(\frac{\partial P}{\partial V}\right)_T + P}\right)\right]^{-1}$$

Which simplifies by applying equation (7-16) to the first derivative of P with respect to V:

$$\left(\frac{\partial P}{\partial x}\right)_T = \left[\underbrace{\underbrace{\left(P + V\underbrace{\left(\frac{\partial P}{\partial V}\right)_T}_{=0}\right)^{-1}}_{1/P}\underbrace{\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial P}\right)}_{=0}}_{=0} + \underbrace{\underbrace{\left(\frac{\partial P}{\partial V}\right)_T}_{=0}\left(2 + V\underbrace{\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial P}\right)}_{=0}\right)}_{=0}\right]^{-1} \tag{7}$$

$$\left(\frac{\partial P}{\partial x}\right)_T = [0]^{-1} = \infty$$

By similar reasoning we can show,

$$\left(\frac{\partial V}{\partial x}\right)_T = \left[\frac{\partial}{\partial V}\left(\frac{\left(\frac{\partial P}{\partial V}\right)_T}{V\left(\frac{\partial P}{\partial V}\right)_T + P}\right)\right]^{-1}$$

Which simplifies by applying equations (7-16) and (7-39) to the first and second derivative of P with respect to V,

$$\left(\frac{\partial V}{\partial x}\right)_T = \left[ \underbrace{\underbrace{\left( P + V \underbrace{\left(\frac{\partial P}{\partial V}\right)_T}_{A_{VV}=0} \right)^{-1}}_{1/P} \underbrace{\left(\frac{\partial^2 P}{\partial V^2}\right)}_{A_{VVV}=0}}_{=0} - \underbrace{\underbrace{\left(\frac{\partial P}{\partial V}\right)_T}_{A_{VV}=0} \underbrace{\left( P + V \underbrace{\left(\frac{\partial P}{\partial V}\right)_T}_{A_{VV}=0} \right)^{2}}_{\left(1/P\right)^2} \left( 2 \underbrace{\left(\frac{\partial P}{\partial V}\right)_T}_{A_{VV}=0} + V \underbrace{\left(\frac{\partial^2 P}{\partial V^2}\right)}_{A_{VVV}=0} \right)}_{=0} \right]^{-1} \quad (8)$$

$$\left(\frac{\partial V}{\partial x}\right)_T = \left[0\right]^{-1} = \infty$$

Plugging equation (7) and (8) back into (6) yields,

$$\left(\frac{\partial^2 P}{\partial (PV)^2}\right)_{T=T_C} = \left[V\infty + P\infty\right]^{-1} = \left[\infty\right]^{-1} = 0$$

Thus, the criteria given in equations (7-16) and (7-39) are satisfied at the critical point in the Amagat Diagram.