Assignment 1 due May 16, 2007

P317

Problems from Carter

1-2) (a) reversible, isobaric heating

(b) irreversible, isothermal, quasistatic expansion

(c) non-quasistatic, irreversible, approximately adiabatic (no time for compression heat flow)

(d) irreversible, non-quasistatic, isochoric cooling

(e) reversible isochoric, isobaric, isothermal

(f) irreversible, non-quasistatic, adiabatic

1-6) Given

P_{TP} (torr)	100	200	300	400
P (torr)	127.9	256.5	385.8	516

Find T. Fit the ratio (P/P_{TP}) vs. P_{TP} to a line: $\frac{P}{P_{TP}} = aP_{TP} + b$ to find $b = 1.27525$

Since $T = \lim_{P_{TP} \to 0} \left(\frac{P}{P_{TP}}\right) T_{TP} = b\,T_{TP} \Rightarrow T = b \cdot 273.16\,K$

$= 348.35K = 75.20°C$

1-9) $T = 0$ at ice point and 100 at steam point

(a) $X = aT + b \Rightarrow X_i = b,\ X_s = 100a + b$ so $a = \frac{X_s - b}{100} = \frac{X_s - X_i}{100}$

$\therefore T = 100\frac{X - X_i}{X_s - X_i}$

(b) $T = a\ln X + b \Rightarrow 0 = a\ln X_i + b,\ 100 = a\ln X_s - a\ln X_i = a\ln\frac{X_s}{X_i}$

$T = \frac{100\cancel{X}}{\ln\frac{X_s}{X_i}} - a\ln X_i = 100\,\frac{\ln(X/X_i)}{\ln(X_s/X_i)}$

P317

Assignment 1 continued

2-6) $P = \frac{RT}{v-b} - \frac{a}{Tv^2}$. At critical pt. $\frac{\partial P}{\partial v} = \frac{\partial^2 P}{\partial v^2} = 0$

$$\rightarrow 0 = \frac{-RT}{(v-b)^2} + \frac{2a}{Tv^3} \quad \text{and} \quad 0 = \frac{2RT}{(v-b)^3} - \frac{6a}{Tv^4}$$

Eliminate T from these two equations to find

$v_c = 3b$. Then sub in to get $T_c = \sqrt{\frac{8a}{27Rb}}$

and $P_c = \frac{1}{12b}\sqrt{\frac{2aR}{3b}}$. These give $\frac{RT_c}{P_c v_c} = \frac{8}{3} = 2.67$

which is the same as the van der Waals equation result, and somewhat below values for real gases

2-8) Dieterici eq^n: $P = \frac{RT}{v-b} e^{-a/RTv}$. $\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b}\left(1+\frac{a}{RTv}\right)e^{-a/RTv}$

$$\beta \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_v \qquad \left(\frac{\partial P}{\partial v}\right)_T = \frac{R}{v-b}\left(-\frac{T}{v-b} + \frac{a}{Rv^2}\right)e^{-a/RTv}$$

$$= +\frac{1}{v}\frac{1+\frac{a}{RTv}}{\frac{T}{v-b} - \frac{a}{Rv^2}} \xrightarrow[T,v\to\infty]{} \frac{1}{v}\frac{1}{\frac{T}{v}} = \frac{1}{T} \quad \text{as for ideal gas}$$

2-11) $\beta = \frac{v-a}{Tv}$, $\kappa = \frac{3(v-a)}{4Pv}$

$$dv = \beta v\, dT - \kappa v\, dP = \frac{v-a}{T}dT - \frac{3(v-a)}{4P}dP$$

Upon integration along a path $(T_i, P_i) \rightarrow (T_f, P_i) \rightarrow (T_f, P_f)$

$$\int \frac{dv}{v-a} = \int_{P_i} \frac{dT}{T} - \frac{3}{4}\int_{T_f} \frac{dP}{P}$$

so $\ln(v-a) = \ln T - \frac{3}{4}\ln P + \text{constant}$

or $\ln\left[P^{3/4}(v-a)\right] = \ln T + \text{constant} = \ln T + \ln A$

exponentiate to find $P^{3/4}(v-a) = AT$ with $A = e^{\text{constant}}$