Homework #2

Solutions

Carter 1.10, 2.7, 2.8, 2.10, 3.8, 3.11

Schroeder 1.19, 1.34

Additional Problem 1

Carter

1.10 $F = 1.8C + 32$; $K = C + 273 \Rightarrow C = K - 273$

- F: Temp in °F
- C: Temp in °C
- K: Temp in K

$F = 1.8(K - 273) + 32$

When are K & F equal? Set $F = K$:

$K = 1.8(K - 273) + 32$

$K = 1.8K - 1.8 \cdot 273 + 32$

$-0.8K = -459.4$

$K = F = 574.25$

2.7

$$\left.\frac{\partial P}{\partial V}\right|_T = \left.\frac{\partial^2 P}{\partial V^2}\right|_T = 0 \quad \text{at the critical point}$$

$$\left.\frac{\partial P}{\partial V}\right|_T = \left.\frac{\partial}{\partial V}\right|_T \left(\frac{RT}{V-b} e^{-a/RTV}\right)$$

$$= -\frac{RT}{(V-b)^2} e^{-a/RTV} + \frac{RT}{V-b} \cdot \frac{+a}{RTV^2} e^{-a/RTV}$$

At the critical point: $0 = -\frac{RT_c}{(V_c-b)^2} e^{-a/RT_cV_c} + \frac{RT_c}{V_c-b} \cdot \frac{a}{RT_c(V_c)^2} e^{-a/RT_cV_c}$

Crossed-out terms cancel.

$$\left.\frac{\partial^2 P}{\partial V^2}\right|_T = \frac{2RT}{(V-b)^3} e^{-a/RTV} - \frac{RT}{(V-b)^2} \cdot \frac{a}{RTV^2} e^{-a/RTV}$$

$$- \frac{RT}{(V-b)^2} \cdot \frac{a}{RTV^2} e^{-a/RTV} + \frac{RT}{V-b}\left[\frac{-2a}{RTV^3} e^{-a/RTV}\right.$$

$$\left. + \frac{a^2}{(RT)^2 V^4} e^{-a/RTV}\right]$$

At critical point:

$$0 = \frac{2RT_c}{(V_c-b)^3} e^{-a/RT_cV_c} - \frac{2RT_c}{(V_c-b)^2} \cdot \frac{a}{RT_cV_c^2} e^{-a/RT_cV_c}$$

$$+ \frac{RT_c}{(V_c-b)}\left[\frac{-2a}{RT_cV_c^3} e^{-a/RT_cV_c} + \frac{a^2}{(RT_c)^2 V_c^4} e^{-a/RT_cV_c}\right]$$

Again, crossed-out terms cancel.

Now we have a system of 2 eqns & 2 unknowns (T_c & V_c).

$$\frac{\partial P}{\partial V} = 0 = \frac{-1}{V_c - b} + \frac{1a}{RT_c V_c^2}$$

$$\frac{1}{V_c - b} = \frac{a}{RT_c V_c^2} \Rightarrow V_c - b = \frac{RT_c V_c^2}{a} \quad (1)$$

$$\frac{\partial^2 P}{\partial V^2} = 0 = \frac{2}{(V_c-b)^2} - \frac{2a}{(V_c-b)RT_c V_c^2} - \frac{2a}{RT_c V_c^3}$$

$$+ \frac{a^2}{(RT_c)^2 V_c^4} \quad (2.)$$

From (1) we see

$$T_c = \frac{(V_c - b)a}{R V_c^2}.$$

Substituting in for T_c from (1):

$$\frac{\partial^2 P}{\partial V^2} = 0 = \frac{2}{(V_c-b)^2} - \frac{2a}{(V_c-b)\cancel{R}\frac{(V_c-b)a}{RV_c^2}\cancel{V_c^2}}$$

$$- \frac{2a}{\cancel{R}\frac{(V_c-b)a}{R\cancel{V_c^2}}V_c^3} + \frac{a^2}{\cancel{R^2}\frac{(V_c-b)^2 a^2}{\cancel{R^2}V_c^4}\cdot\cancel{V_c^4}}$$

$$0 = \frac{2}{\cancel{(V_c-b)^2}} - \frac{2}{\cancel{(V_c-b)^2}} - \frac{2}{(V_c-b)V_c} + \frac{1}{(V_c-b)^2}$$

$$0 = \frac{-2}{(V_c - b)V_c} + \frac{1}{(V_c - b)^2}$$

$$\frac{2}{V_c} = \frac{1}{V_c - b} \qquad \frac{V_c}{2} = V_c - b \qquad -\frac{1}{2}V_c = -b$$

$$\boxed{V_c = 2b}$$

$$T_c = \frac{(V_c - b)}{R V_c^2} a = \frac{2b - b}{R(2b)^2} a = \frac{ba}{4Rb^2}$$

$$\boxed{T_c = \frac{a}{4Rb}}$$

$$P_c = \frac{R T_c}{V_c - b} e^{-a/R T_c V_c} = \frac{R \frac{a}{4Rb}}{2b - b} e^{-a/R \frac{a}{4Rb} \cdot 2b}$$

$$P_c = \frac{a}{4b^2} e^{-2} = \boxed{\frac{a}{4b^2 e^2}}$$

$$\frac{R T_c}{P_c V_c} = \frac{R \cdot \frac{a}{4Rb}}{\frac{a}{4b^2 e^2} \cdot 2b} = \frac{4be^2}{8b} = \frac{e^2}{2}$$

$$= \boxed{3.69}$$

Fairly close to experimental values.
Closest to CO_2.

2.8 a. $\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$= \frac{1}{V} \cdot \frac{-1}{\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T}$$

But $\left.\frac{\partial T}{\partial P}\right|_V = \frac{1}{\left.\frac{\partial P}{\partial T}\right|_V}$

So:

$$\beta = -\frac{1}{V} \frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial V}\right)_T}$$

$$P = \frac{RT}{V-b} e^{-a/RTV}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} e^{-a/RTV} + \frac{RT}{V-b}\left(\frac{a}{RVT^2}\right) e^{-a/RTV}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} e^{-a/RTV} + \frac{RT}{V-b}\left(\frac{a}{RTV^2}\right) e^{-a/RTV}$$

$$\beta = -\frac{1}{V} \frac{\frac{R}{V-b} e^{-a/RTV} + \frac{RT}{V-b}\left(\frac{a}{RVT^2}\right) e^{-a/RTV}}{-\frac{RT}{(V-b)^2} e^{-a/RTV} + \frac{RT}{V-b}\frac{a}{RTV^2} e^{-a/RTV}}$$

$$\beta = -\frac{1}{V} \frac{1 + \frac{a}{RVT}}{-\frac{T}{V-b} + \frac{a}{RV^2}} = \boxed{\frac{(V-b)RVT + a(V-b)}{RV^2T^2 - Ta(V-b)}}$$

b. $\lim_{T\to\infty,\ V\to\infty} \beta$

$$= \lim_{\substack{T\to\infty,\\ V\to\infty}} \frac{1 + a/RVT}{T\left(\frac{V}{V-b}\right) - \frac{a}{RV}} = \frac{1}{T\cdot 1 + 0}$$

$$= \frac{1}{T}$$

(Rewriting β in this form makes limits easier)

For ideal gas, $\beta = \frac{1}{T}$.

This means that our β becomes ... closer to the ideal gas β for high T & V.

2.10:

$$\beta = \frac{2bT}{V} \qquad \kappa = \frac{a}{V}$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

I am using the book's notation here.

$\left(\frac{\partial V}{\partial T}\right)_P$ = partial of V with respect to T at constant P

$$\frac{2bT}{V} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \frac{a}{V} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$2bT = \left(\frac{\partial V}{\partial T}\right)_P \qquad -a = \left(\frac{\partial V}{\partial P}\right)_T$$

Anti-derivative $\Longrightarrow$ $\Longrightarrow$

$$V = \frac{2bT^2}{2} + \alpha(P) + C_1 \qquad V = -aP + \beta(T) + C_2$$

Comparing these two expressions, we see that

$\alpha(P) = -aP$ & $\beta(T) = bT^2$ ($C_1 = C_2$ also)

$$V = bT^2 - aP + C$$

$$\boxed{V - bT^2 + aP = C}$$

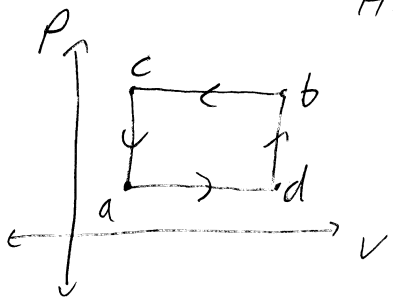
3.8 $W = -\int P\,dV$

$+P\,dV$ = work done BY the gas

$-P\,dV$ = work done ON the gas by the environment

If we define W as $-\int P\,dV$, we can define ΔU as $Q + W$

↑ Heat added to gas



$\Delta U_{ab} = 80 - 30 = 50\ J$

a. path adb

$\Delta U_{ab} = Q - 10 = 50$

$Q = 60\ J$

b. $\Delta U_{ba} = -50\ J = 20 + Q$

$Q = -70\ J$

c. $U_a = 0$, $U_d = 40$

$\Delta U_{ad} = 40 = Q + W$

$W = W_{adb} = -10\ J$

$40 = Q - 10$

$Q_{ad} = 50\ J$

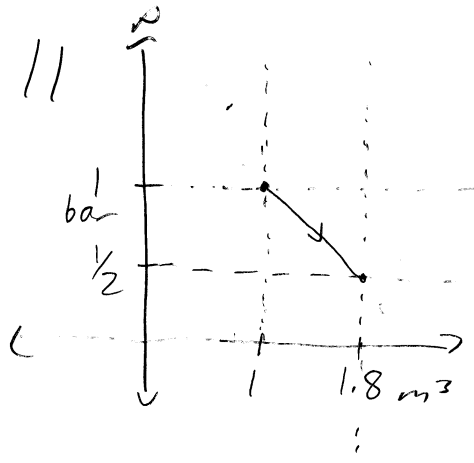
All the work done by the gas along adb is done along ad (since it is over this interval that the volume changes.) $\Rightarrow W_{ad} = W_{adb}$

$W_{db} = 0$

$\Delta U_{db} = U_b - U_d = 50 - 40 = 10\ J$, $10\ J = Q_{db} + 0$

$\Delta U_{db} = Q_{db} + W_{db}$ $W_{db} = 0$ $Q_{db} = 10$

3.11



a. $V = AP + B$

(1.) $1 = 1 \cdot A + B$

(2.) $1.8 = \frac{1}{2}A + B = (A+B) - \frac{1}{2}A$

Plugging A into (1.) yields $1.8 = 1 - \frac{1}{2}A$

$-\frac{1}{2}A = 0.8$

$A = -1.6 \frac{m^3}{bar}$

$1 = 10^5 - 1.6 \cdot 10^5 + B$

$B = 1 + 1.6\ m^3$

$B = 2.6\ m^3$

$A = -1.6 \cdot 10^{-5}\ m^3/Pa$

b. $P_1 V_1 = nRT_1$

$P_2 V_2 = nRT_2$

$\frac{T_1}{T_2} = \frac{P_1 V_1}{P_2 V_2} \Rightarrow \frac{300}{T_2} = \frac{1 \cdot 1}{1.8 \cdot 0.5}$

$T_2 = 270\ K$

c. Work done BY the gas $= +\int P\,dV = -W$

$-W = \int_{V_i}^{V_f} \frac{V-B}{A}\,dV = \left[\frac{V^2}{2A} - \frac{BV}{A}\right]_1^{1.8}$ A & B defined above

$-W = +6 \cdot 10^4\ J$

d. $\Delta U = 800 \cdot \Delta T = 800\,(270 - 300)$

$= -24{,}000\ J$

$\Delta U = Q + W$

$-24{,}000 = Q - 6 \cdot 10^4$

$Q = 3.6 \cdot 10^4\ J$

Schroeder

1.19

$$v_{rms} = \sqrt{\frac{3kT}{m}}$$

$$v_{O_2} = \sqrt{\frac{3kT}{m_{O_2}}} \qquad v_H = \sqrt{\frac{3kT}{m_H}}$$

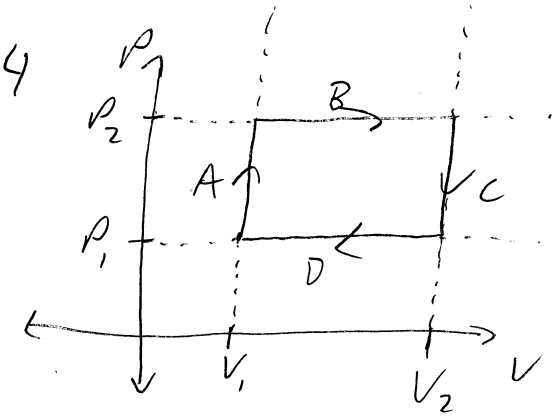
$$\frac{v_{O_2}}{v_H} = \sqrt{\frac{\cancel{3kT}/m_{O_2}}{\cancel{3kT}/m_H}} = \sqrt{\frac{m_H}{m_{O_2}}}$$

$$m_H = \frac{1}{16} m_{O_2} \Longrightarrow \frac{v_{O_2}}{v_H} = \sqrt{\frac{1}{16}} = \frac{1}{4}$$

$$v_{O_2} = \frac{v_H}{4} \qquad (v_H = 4 v_{O_2})$$

The hydrogen molecules will, on average, be 4 times faster.

1.34



Diatomic $\Rightarrow U = \frac{5}{2}NkT$

(5 degrees of freedom)

$PV = nRT = NkT$

a. A: $W = 0$ $\Delta U = Q + W = Q$

$\Delta U = \frac{5}{2}Nk(T_f - T_i) = \frac{5}{2}Nk\left(\frac{P_2V_1}{Nk} - \frac{P_1V_1}{Nk}\right)$

$\Delta U = Q = \frac{5}{2}(P_2 - P_1)V_1$

B: $W = -\int P\,dV = -P_2(V_2 - V_1)$

$\Delta U = \frac{5}{2}Nk\left(\frac{P_2V_2}{Nk} - \frac{P_2V_1}{Nk}\right) = \frac{5}{2}P_2(V_2 - V_1)$

$\Delta U = Q + W$

$Q = \Delta U - W = \frac{7}{2}P_2(V_2 - V_1)$

C: $W = 0$

$\Delta U = -\frac{5}{2}(P_2 - P_1)V_2$

$Q = -\frac{5}{2}(P_2 - P_1)V_2$

- Reverse of A, except at $V = V_2$.

D: $W = -\int P\,dV = -P_1(V_1 - V_2)$

$\Delta U = \frac{5}{2}P_1(V_1 - V_2)$

$Q = \frac{7}{2}P_1(V_1 - V_2)$

b. A: Add heat while holding piston fixed.

B: Let piston out while adding heat such that P remains constant.

C: Exhaust heat (cool the gas) while holding the piston in place

D: Push the piston in while exhausting heat such that P remains constant

c.

	W	ΔU	Q
A	0	$\frac{5}{2} V_1 (P_2 - P_1)$	$\frac{5}{2} V_1 (P_2 - P_1)$
B	$-P_2 (V_2 - V_1)$	$\frac{5}{2} P_2 (V_2 - V_1)$	$\frac{7}{2} P_2 (V_2 - V_1)$
C	0	$-\frac{5}{2} V_2 (P_2 - P_1)$	$-\frac{5}{2} V_2 (P_2 - P_1)$
D	$P_1 (V_2 - V_1)$	$-\frac{5}{2} P_1 (V_2 - V_1)$	$-\frac{7}{2} P_1 (V_2 - V_1)$
Net	$-(P_2 - P_1)(V_2 - V_1)$	0	$(P_2 - P_1)(V_2 - V_1)$

$\Delta U_{net} = 0$, as it should, since U depends only on the state of the gas, and the gas is in the same state after a full cycle.

W done on the gas is negative; since $W = -\int P dV$ = negative of the area under the PV curve, this makes sense.

Q_{net} is positive, which makes sense since

$$Q_{net} + W_{net} = \Delta U_{net} = 0$$

$$\Rightarrow$$

$$Q_{net} = -W_{net}$$ & W_{net} is negative.

The entire cycle has the effect of adding heat to cause the gas to do work on its environment. It is a heat engine.

Additional Problems

1. a. Work is the same, since it depends only on the P-V diagram. (The VdW gas is stated as having an identical PV diagram)

b. $W_{net} = -(P_2 - P_1)(V_2 - V_1)$

$Q_{net} = (P_2 - P_1)(V_2 - V_1)$

$\Delta U_{net} = 0$

(ΔU_{net} around a closed cycle is always 0, so we can use this to easily find Q_{net}.)