

Meg Noah  
 Statistical Physics  
 95.521  
 Sept. 15, 2008  
 Problem Set #1

10/10

- 1.1 Show that for a quasistatic adiabatic process in a perfect gas, with specific heats,  $PV^\gamma = \text{const}$  where  $\gamma = C_p/C_v$

$$dQ = 0 \quad (\text{adiabatic})$$

$$PV = RT \quad (1.5 \text{ equation for perfect gas})$$

$$dQ = dE + PdV = 0 \quad (1.17)$$

$$C_v dT + PdV = 0 \quad (1.18a)$$

using  $P = (RT)/V$  from eq. of state for a perfect gas

$$C_v dT + \frac{RT}{V} dV = 0$$

$$\text{using } C_p - C_v = R \quad (1.20)$$

$$C_v dT + \left( \frac{C_p - C_v}{V} \right) T dV = 0$$

$$\frac{dT}{T} = \frac{dV}{V} \left( 1 - \frac{C_p}{C_v} \right)$$

$$\frac{dT}{T} = (1-\gamma) \frac{dV}{V}$$

$$\int \frac{dT}{T} = (1-\gamma) \int \frac{dV}{V}$$

$$\ln T + \text{cnst} = (1-\gamma) \ln V$$

$$\ln T + \ln C = (1-\gamma) \ln V$$

$$\ln CT = \ln V^{(1-\gamma)}$$

$$CT = V^{(1-\gamma)}$$

$$\frac{CPV}{R} = V^{(1-\gamma)}$$

$$PV^\gamma = CR = \text{cnst}$$

(a)

let cnst =  $\ln C$

1.2 The molar energy of a monatomic gas which obeys

Van der Waal's equation:

$$E = \frac{3}{2} RT - \frac{a}{V}$$

$V$  = molar volume @  $T$     $a = \text{const}$

$$V_1, T_1 \Rightarrow V_2, T_2 = ?$$

$$\delta Q = 0$$

adiabatic expansion:  $\delta Q = 0 \quad \Delta E = 0$

$$\Delta E = E_2 - E_1 = \left( \frac{3}{2} RT_2 - \frac{a}{V_2} \right) - \left( \frac{3}{2} RT_1 - \frac{a}{V_1} \right) = 0$$

$$\frac{3}{2} R(T_2 - T_1) = \frac{1}{a} \left( \frac{1}{V_2} - \frac{1}{V_1} \right)$$

$$T_2 = T_1 + \frac{2a}{3R} \left( \frac{1}{V_2} - \frac{1}{V_1} \right)$$

1.3 Calculate the work done against 1 mole of a perfect gas in an adiabatic quasistatic compression from  $V_1$  to  $V_2$ .

$$\delta Q = 0$$

$$dE = dW = -PdV$$

$$W = - \int_{V_1}^{V_2} PdV$$

$$C_V dT = -PdV \quad (1.18a)$$

$$W = \int_{T_1}^{T_2} C_V dT = C_V (T_2 - T_1) = \frac{C_V}{R} (P_2 V_2 - P_1 V_1)$$

$$\frac{R}{C_V} W = P_2 V_2 - P_1 V_1 =$$

$$\frac{(C_P - C_V)}{C_V} W = P_2 V_2 - P_1 V_1$$

$$(Y-1) W = P_2 V_2 - P_1 V_1$$

$$W = \frac{1}{(Y-1)} (P_2 V_2 - P_1 V_1)$$

(2)

1.4 Enthalpy is  $H \equiv E + PV$ . Express heat capacity at  $P = \text{constant}$  in terms of enthalpy.

$$dQ = dE + PdV = dH$$

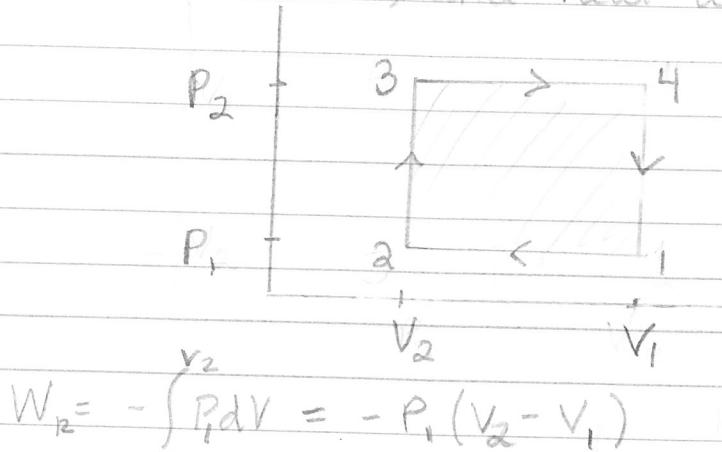
$$dH = dE + PdV + Vdp \stackrel{P=\text{const}}{=} dQ + Vdp \stackrel{P=\text{const}}{=} dQ$$

$$C_p = \left( \frac{\partial Q}{\partial T} \right)_p = \left( \frac{\partial H}{\partial T} \right)_p$$

1.5 One mole of a perfect gas performs a quasistatic cycle which consists of the following four successive stages.

- (i) from  $(P_1, V_1)$  -  $\Delta P = 0 \rightarrow (P_1, V_2)$
- (ii) from  $(P_1, V_2)$  -  $\Delta V = 0 \rightarrow (P_2, V_2)$
- (iii) from  $(P_2, V_2)$  -  $\Delta P = 0 \rightarrow (P_2, V_1)$
- (iv) from  $(P_2, V_1)$  -  $\Delta V = 0 \rightarrow (P_1, V_1)$

Find work done, and heat absorbed.



$$W_{12} = - \int_{V_1}^{V_2} P_1 dV = -P_1(V_2 - V_1)$$

$$W_{23} = - \int_{V_2}^{V_3} P_2 dV = 0$$

$$W_{34} = - \int_{V_2}^{V_1} P_2 dV = -P_2(V_1 - V_2) = P_2(V_2 - V_1)$$

$$W_{41} = - \int_{V_1}^{V_2} P_1 dV = 0$$

$$W = W_{12} + W_{23} + (W_{34} + W_{41}) = -P_1(V_2 - V_1) + P_2(V_2 - V_1)$$

$$W = (P_2 - P_1)(V_2 - V_1)$$

$$\Delta E = 0 = Q + W$$

$$\therefore Q = -W = -(P_2 - P_1)(V_2 - V_1) = (P_1 - P_2)(V_2 - V_1)$$

- 1.6 i)  $(T_1, V_1) - \Delta V = 0 \rightarrow (T_2, V_1)$   
ii)  $(T_2, V_1) - \Delta T = 0 \rightarrow (T_2, V_2)$   
iii)  $(T_2, V_2) - \Delta V = 0 \rightarrow (T_1, V_2)$   
iv)  $(T_1, V_2) - \Delta T = 0 \rightarrow (T_1, V_1)$

$$W = - \int P dV \quad PV = RT$$

$$P = \frac{RT}{V}$$

$$W = - \int \frac{RT dV}{V} =$$

$$W_{12} = - \int_{V_1}^{V_2} \frac{RT dV}{V} = 0$$

$$W_{23} = - \int_{V_1}^{V_2} \frac{RT_2 dV}{V} = -RT_2 \ln\left(\frac{V_2}{V_1}\right)$$

$$W_{34} = - \int_{V_2}^{V_1} \frac{RT dV}{V} = 0$$

$$W_{41} = - \int_{V_2}^{V_1} \frac{RT_1 dV}{V} = -RT_1 \ln\left(\frac{V_1}{V_2}\right) = RT_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$W = W_{12} + W_{23} + W_{34} + W_{41} = R(T_1 - T_2) \ln\left(\frac{V_2}{V_1}\right) \quad (2)$$

$$Q = -W = R(T_2 - T_1) \ln\left(\frac{V_2}{V_1}\right)$$

1.7 Calculate the change in internal energy when 1 mole of a liquid water at 1 atm and 100°C is evaporated to water vapour at the same pressure and temperature, given that the molar volumes of the liquid and the vapour under these conditions are  $18.8 \text{ cm}^3/\text{mol}$  and  $3.02 \cdot 10^4 \text{ cm}^3/\text{mol}$ , and that the latent heat of evaporation is  $4.06 \cdot 10^4 \text{ J/mol}$ .

$$P_1 = 1 \text{ atm}$$

$$P_2 = 1 \text{ atm}$$

$$T_1 = 100^\circ\text{C} = 373.15 \text{ K}$$

$$T_2 = 373.15 \text{ K}$$

$$\Delta Q = \cancel{P} \cancel{V} \cancel{\Delta T}$$

$$\text{Since } PV = RT \Rightarrow V_1 = V_2$$

$$\Delta Q = \left( \frac{4.06 \cdot 10^4 \text{ J}}{\text{mol}} \right) (1 \text{ mol}) = 4.06 \cdot 10^4 \text{ J} = 40600 \text{ Nm}$$

$$-PdV = -(1 \text{ atm}) (18.8 \text{ cm}^3 - 3.02 \cdot 10^4 \text{ cm}^3)$$

$$= \left( \frac{101325 \text{ N}}{\text{m}^2} \right) (30,181.2 \text{ cm}^3) \left( \frac{1 \text{ m}}{100 \text{ cm}} \right)^3 = 3058 \text{ Nm}$$

$$\Delta E = Q + W = \Delta Q + PdV = 40600 \text{ Nm} - 3058 \text{ Nm}$$

$$= 37542 \text{ J}$$

$$= 3.754 \cdot 10^4 \text{ J} \quad (\text{for 1 mole})$$

(2)