Homework 01

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1.1

 \mathbf{a}

From the first law,

$$dQ = dE - dW. (1.1.1)$$

Hence,

$$Q_{h} = \int \left(\frac{\partial E}{\partial \Theta} d\Theta + P dV \right), \quad (1.1.2) \qquad \frac{V}{V_{0}} = e^{-\frac{1}{Nk_{B}} \int_{\Theta_{0}}^{\Theta} \frac{1}{\tau} \frac{\partial E}{\partial \Theta} \Big|_{\tau} d\tau}. \quad (1.1.11)$$

$$= \int \frac{Nk_{B}\Theta_{h}}{V} dV, \quad (1.1.3) \quad \mathbf{c}$$

$$= Nk_B \Theta_h \ln \left(\frac{V_2}{V_1}\right). \tag{1.1.4}$$
 By definition,

$$Q_c = Nk_B\Theta_c \ln\left(\frac{V_3}{V_4}\right). \tag{1.1.5}$$

For 1.1.5, heat is being expelled, hence From equations 1.1.4 and 1.1.5, the minus sign (evident in swapping the bounds of integration).

b

From the first law,

$$dE = -P \, dV \,, \tag{1.1.6}$$

$$\frac{\partial E}{\partial \Theta} d\Theta = -P dV. \qquad (1.1.7)$$

Assuming an ideal gas,

$$P = \frac{Nk_B\Theta}{V}. (1.1.8)$$

Plugging this into 1.1.7 gives

Take the first law:

$$\frac{1}{\Theta} \frac{\partial E}{\partial \Theta} d\Theta = -Nk_B \frac{dV}{V}. \qquad (1.1.9) \qquad dQ = dE - dW. \qquad (1.2.1)$$

1.2

Integrating both sides from (V_0, Θ_0) to (V,Θ) gives

$$\int_{\Theta_0}^{\Theta} \frac{1}{\tau} \left. \frac{\partial E}{\partial \Theta} \right|_{\tau} d\tau = -Nk_B \ln\left(\frac{V}{V_0}\right), \tag{1.1.10}$$

$$\frac{V}{V_0} = e^{-\frac{1}{Nk_B} \int_{\Theta_0}^{\Theta} \frac{1}{\tau} \frac{\partial E}{\partial \Theta} \Big|_{\tau} d\tau}.$$
 (1.1.11)

(1.1.5)
$$\eta \equiv \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}.$$
 (1.1.12)

$$1 - \frac{Q_c}{Q_h} = 1 - \frac{\Theta_c \ln(V_3/V_4)}{\Theta_h \ln(V_2/V_1)} \quad (1.1.13)$$

Additionally, from 1.1.11, $\ln(V_2/V_1) =$ $\ln(V_3/V_4)$. Thus

$$\eta = 1 - \frac{\Theta_c}{\Theta_h}.\tag{1.1.14}$$

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If one uses (T, V) as the independent 1.3 variables, then

$$dQ = \frac{\partial E}{\partial T} dT + \left(\frac{\partial E}{\partial V} + P\right) dV,$$
(1.2.2)

$$= C_V dT + \left(\frac{\partial E}{\partial V} + P\right) dV. \quad (1.2.3)$$

b

Finding an expression for dS, if follows from the second law that

$$dS = \frac{dQ}{T},$$

$$= \frac{C_V}{T} dT + \left(\frac{1}{T} \frac{\partial E}{\partial V} + \frac{P}{T}\right) dV.$$
(1.2.5)

By definition of an exact differential,

$$\frac{\partial S}{\partial V} = \frac{1}{T} \frac{\partial E}{\partial V} + \frac{P}{T},\tag{1.2.6}$$

$$\frac{\partial S}{\partial T} = \frac{C_V}{T}.\tag{1.2.7}$$

Additionally

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V},\tag{1.2.8}$$

SO

$$\frac{\partial}{\partial V} \frac{C_V}{T} = \frac{\partial}{\partial T} \left(\frac{1}{T} \frac{\partial E}{\partial V} + \frac{P}{T} \right), \quad (1.2.9)$$

$$0 = -\frac{1}{T^2} \frac{\partial E}{\partial V} - \frac{P}{T^2} + \frac{1}{T} \frac{\partial P}{\partial T}, \quad (1.2.10)$$

$$= \frac{\partial E}{\partial V} + P - T \frac{\partial P}{\partial T}, \quad (1.2.11)$$

$$\frac{\partial E}{\partial V} = T \frac{\partial P}{\partial T} - P. \tag{1.2.12}$$

 \mathbf{c}

For an ideal gas,

$$\frac{\partial E}{\partial V} = \frac{Nk_BT}{V} - P = 0. \tag{1.2.13}$$

Thus the internal energy cannot depend on V, and is only a function of T. However, since no consideration was made pertaining to the particle number, N, the internal energy could still depend on N. Therefore E = E(T, N).

From the first law,

$$dE = -P \, dV - S \, dT + \mu \, dN \,, \quad (1.3.1)$$

where

$$P \equiv -\frac{\partial E}{\partial V},\tag{1.3.2}$$

$$S \equiv -\frac{\partial E}{\partial T},\tag{1.3.3}$$

$$\mu \equiv \frac{\partial E}{\partial N}.\tag{1.3.4}$$

The Maxwell relations mentioned are derived as follows:

$$\frac{\partial \mu}{\partial T} = \frac{\partial^2 E}{\partial T \partial N} = -\frac{\partial S}{\partial N}.$$
 (1.3.5)

$$\frac{\partial S}{\partial V} = -\frac{\partial^2 E}{\partial T \partial V} = \frac{\partial P}{\partial T}.$$
 (1.3.6)

Inverting these gives the requested relations:

$$\frac{\partial T}{\partial \mu} = -\frac{\partial N}{\partial S},\tag{1.3.7}$$

$$\frac{\partial P}{\partial T} = \frac{\partial S}{\partial V}.$$
 (1.3.8)

1.4

The Helmholtz Free Energy is given by

(1.2.12)
$$A = T_0 \ln\left(\frac{V}{V_0}\right) - T\frac{V}{V_0} \left(\frac{T}{T_0}\right)^a. \quad (1.4.1)$$

b

The equation of state is found by using the Maxwell relation

$$-P = \frac{\partial A}{\partial V} = \frac{T_0}{V} - \frac{T}{V_0} \left(\frac{T}{T_0}\right)^a. \quad (1.4.2)$$

This can be rewritten more simply as

$$PV = ST - T_0.$$
 (1.4.3)

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 \mathbf{c}

From 1.4.3,

$$W = -\int_{V_a}^{V_b} P \, dV , \qquad (1.4.4)$$

$$= \int_{V_a}^{V_b} \frac{T_0}{V} - \frac{T_a}{V_0} \left(\frac{T_a}{T_0}\right)^a dV , \quad (1.4.5)$$

$$= T_0 \ln\left(\frac{V_b}{V_a}\right) - \frac{(V_b - V_a)T_a}{V_0} \left(\frac{T_a}{T_0}\right)^a \quad (1.4.6)$$