

Physics 425, Spring 2009

Quiz - 4
March 10, Tuesday

Name: _____ ID: _____

(books and notes are not allowed)

Planck constant: $h = 6.63 \times 10^{-34} \text{ J s}$

Boltzmann constant: $k = 1.38 \times 10^{-23} \text{ J/K}$

Avogadro number: $N_a = 6.02 \times 10^{23}$

Gas constant: $R = 8.31 \text{ J/K/mol}$

$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$

$T (\text{K}) = T (^{\circ} \text{C}) + 273.16$

$E = f/2 kT$

$TdS = dE + dW$

$\log(e) = 0.43$

Maxwell relations:

$$\left. \frac{\partial T}{\partial V} \right|_S = - \left. \frac{\partial P}{\partial S} \right|_V$$

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial P}{\partial T} \right|_V$$

$$\left. \frac{\partial V}{\partial S} \right|_P = \left. \frac{\partial T}{\partial P} \right|_S$$

$$\left. \frac{\partial S}{\partial P} \right|_T = - \left. \frac{\partial V}{\partial T} \right|_P$$

Note:

- Not all the above constants or relations are useful.
- Explain how the result is obtained. Generous partial credit will be given to correct steps and explanations even if the final result may be erroneous.

1. Answer the following questions:
 - (a) The enthalpy is defined as $H = E + PV$. Write the expression for dH using the first law.
 - (b) From (a), find $\frac{\partial H}{\partial S}|_P$ and $\frac{\partial H}{\partial P}|_S$
 - (c) Suppose that a thermodynamic system evolves quasi-statically with its enthalpy H conserved. When the pressure of the system changes by a small amount ΔP , what is the change in its entropy ΔS as a function of T , V , and ΔP ?

2. A particular gas is described by such an equation of state: $PV^2 = aT$, where a is a constant. For this gas, the heat capacity at constant volume C_V is constant. When the gas evolves quasi-statically from the initial state of temperature T_i and volume V_i to the final state of temperature T_f and volume V_f .
 - (a) Find the change in its entropy ΔS .
 - (b) Find the change in its internal energy ΔE .

Key to solutions:

1. (a) Differentiating H , we get $dH = dE + PdV + VdP$. From the first law $TdS = dE + PdV$. We get $dH = TdS + VdP$.
 - (b) From (a), dH is a function of independent variables dS and dP , so

$$\frac{\partial H}{\partial S}|_P = T, \frac{\partial H}{\partial P}|_S = V$$
 - (c) If H is conserved, $dH = 0$. From (b), $dH = TdS + VdP = 0$. So $dS = -V/T dP$. If P changes by a small amount $\Delta P \sim dP$, S also changes by $\Delta S = -V/T \Delta P$. Here “small amount” means that you do not need integrate, but use approximations $\Delta P \sim dP$ and $\Delta S \sim dS$

2. In this problem, it is seen that we are asked to find the expression of S and E as functions of independent variables T and V . We first should find the expressions for dS and dE as functions of dT and dV , and then integrate from the initial to the final state over T and V .

(a) we may directly write $dS = \frac{\partial S}{\partial T}|_V dT + \frac{\partial S}{\partial V}|_T dV$

Note that $\frac{\partial S}{\partial T}|_V = \frac{1}{T} \frac{T \partial S}{\partial T}|_V = \frac{C_V}{T}$. Using the Maxwell relations, $\frac{\partial S}{\partial V}|_T = \frac{\partial P}{\partial T}|_V$.

Further, from the equation of state $PV^2 = aT$, $\frac{\partial P}{\partial T}|_V = \frac{a}{V^2}$. Therefore,

$$dS = \frac{C_V}{T} dT + \frac{a}{V^2} dV, \text{ and } \Delta S = \int_i^f dS = \int_{T_i}^{T_f} \frac{C_V}{T} dT + \int_{V_i}^{V_f} \frac{a}{V^2} dV = C_V \ln \frac{T_f}{T_i} - a \left(\frac{1}{V_f} - \frac{1}{V_i} \right)$$

(b) we may derive dE using the first law $dE = TdS - PdV$, now that dS is known.

From the expression of dS in (a), we get :

$$dE = T \left(\frac{C_V}{T} dT + \frac{a}{V^2} dV \right) - PdV = C_V dT + \left(\frac{aT}{V^2} - P \right) dV = C_V dT$$

Note here the dV terms cancel! Therefore,

$$\Delta E = \int_i^f dE = \int_{T_i}^{T_f} C_V dT = C_V (T_f - T_i).$$

The internal energy may also be derived in a different way by directly writing

$$dE = \left. \frac{\partial E}{\partial T} \right|_V dT + \left. \frac{\partial E}{\partial V} \right|_T dV$$

From the first law, $dE = TdS - PdV$, if V is constant, then $dE = TdS$, so

$$\left. \frac{\partial E}{\partial T} \right|_V = \frac{T \partial S}{\partial T} \Big|_V = C_V. \text{ The other partial derivative is given as } \left. \frac{\partial E}{\partial V} \right|_T = T \left. \frac{\partial P}{\partial T} \right|_V - P,$$

which is a general relation derived from the thermodynamic law and mathematical properties of exact differentials (see class notes for this). For this particular system

with the given made-up equation of state, it is easily found that $\left. \frac{\partial E}{\partial V} \right|_T = T \left. \frac{\partial P}{\partial T} \right|_V - P = 0$.

In other words, the internal energy in this gas only depends on temperature, just like in the case of an ideal gas. Therefore, $dE = C_V dT$, and $\Delta E = C_V (T_f - T_i)$.

