Planck constant: $h = 6.63 \times 10^{-34}$ J s,
Boltzmann constant: $k = 1.38 \times 10^{-23}$ J/K
Avogadro number: $N_a = 6.02 \times 10^{23}$
Gas constant: $R = 8.31$ J/K/mol
1 eV = $1.6 \times 10^{-19}$ J
$T$ (K) = $T$ ($^0$C) + 273.16
$E = f/2 kT$
$T dS = dE + dW$
$log(e) = 0.43$

Maxwell relations:
\[
\frac{\partial T}{\partial V} \bigg|_S = -\frac{\partial P}{\partial S} \bigg|_V \\
\frac{\partial S}{\partial V} \bigg|_T = \frac{\partial P}{\partial T} \bigg|_V \\
\frac{\partial V}{\partial S} \bigg|_P = \frac{\partial T}{\partial P} \bigg|_S \\
\frac{\partial S}{\partial P} \bigg|_T = -\frac{\partial V}{\partial T} \bigg|_P
\]

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 $\Delta P$, what is the change in its entropy $\Delta S$ as a function of $T$, $V$, and $\Delta P$?

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 $\Delta S$.

(b) Find the change in its internal energy $\Delta E$.

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 $\frac{\partial S}{\partial T} |_V = \frac{1}{T} \frac{T dS}{dT} |_V = \frac{C_V}{T}$. 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,

$$dS = \frac{C_V}{T} dT + \frac{a}{V^2} dV$$

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:

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

Note here the $dV$ terms cancel! Therefore,

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

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

$$dE = \frac{\partial E}{\partial T} \bigg|_V \, dT + \frac{\partial E}{\partial V} \bigg|_T \, dV$$

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

$$\frac{\partial E}{\partial T} \bigg|_V = \frac{T \, dS}{\partial T} \bigg|_V = C_V.$$ The other partial derivative is given as

$$\frac{\partial E}{\partial V} \bigg|_T = T \frac{\partial P}{\partial T} \bigg|_V - P,$$

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

$$\frac{\partial E}{\partial V} \bigg|_T = T \frac{\partial P}{\partial T} \bigg|_V - P = 0.$$

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 $\Delta E = C_V (T_f - T_i)$. 