| **Problems set # 5** | Physics 303 | October 7, 2014 |

1. *(i)* Show that the entropy change in the cyclic process of an ideal gas, that is represented by a rectangle in the (P, V) diagram, is zero. *(ii)* Show that the entropy change in the cyclic process of an ideal gas that include an isobar, an isochore, and an isotherm is zero. See Fig. 1.

Solution: *(i)* In the isobatic process of an ideal gas, the infinitesimal amount of heat is given by $\delta Q = dU + PdV = C_V dT + PdV$. From the equation of state of the ideal gas, $PV = nRT$, it follows that $T = \frac{PV}{nR}$ and so $dT = \frac{PdV}{nR}$. Substitute these expressions into $dS = \delta Q/T$, to obtain $dS = \frac{C_V PdV/(nR) + PdV}{PV/(nR)} = (C_V + nR)\frac{dV}{V} = C_P \frac{dV}{V}$. In the isochoric process of the ideal gas, the heat exchange is $\delta Q = C_V dT = C_V \frac{VdP}{nR}$, and so $dS = \frac{\delta Q}{T} = C_V \frac{dP}{P}$. For the cyclic process in the left panel of Fig. 1, $\Delta S_{AB} = \int_{P_1}^{P_2} C_V \frac{dP}{P} = C_V \ln\frac{P_2}{P_1} > 0$, $\Delta S_{CD} = C_V \ln\frac{P_1}{P_2} = -\Delta S_{AB}$, $\Delta S_{BC} = \int_{V_1}^{V_2} C_P \frac{dV}{V} = C_P \ln\frac{V_2}{V_1} > 0$, and $\Delta S_{DA} = C_P \ln\frac{V_1}{V_2} = -\Delta S_{BC}$. The total entropy change $\Delta S = \Delta S_{AB} + \Delta S_{BC} + \Delta S_{CD} + \Delta S_{DA} = 0$, as it should be. *(ii)* Using the results of *(i)* it follows that $\Delta S_{BC} = C_P \ln\frac{V_2}{V_1} > 0$ and $\Delta S_{CD} = C_V \ln\frac{P_1}{P_2} < 0$. In the isothermal process of an ideal gas $dU = 0$ thus $\delta Q = PdV$ and $dS = \frac{\delta Q}{T} = \frac{PdV}{T} = nR\frac{dV}{V}$. This yields $\Delta S_{DB} = nR \ln\frac{V_1}{V_2} < 0$. Using the equation of state of the ideal gas, on the ends of the isotherm you find $P_1/P_2 = V_1/V_2 \Rightarrow \Delta S_{CD} = C_V \ln\frac{V_1}{V_2}$. The total entropy change over the cycle is $\Delta S = \Delta S_{BC} + \Delta S_{CD} + \Delta S_{DB} = (C_P - C_V - nR) \ln\frac{V_2}{V_1} = 0$, as it should be.

2. Calculate the entropy of a perfect gas as a function of (V, T) by integration using $S = \delta Q/T$.

Solution: Define $S(V_0, T_0) = S_0$ as a reference point and calculate the entropy $S(V, T)$ via the integral of $\delta Q/T$ over a path $(V_0, T_0) \to (V, T)$, that is, $S(V, T) = S_0 + \int_{(V_0, T_0)}^{(V,T)} \frac{\delta Q}{T}$. As the the entropy is a state function, its value does not depend on the path. Hence you can choose the most convenient path, *e.g.*, $(V_0, T_0) \to (V_0, T) \to (V, T)$. During the first stage only the
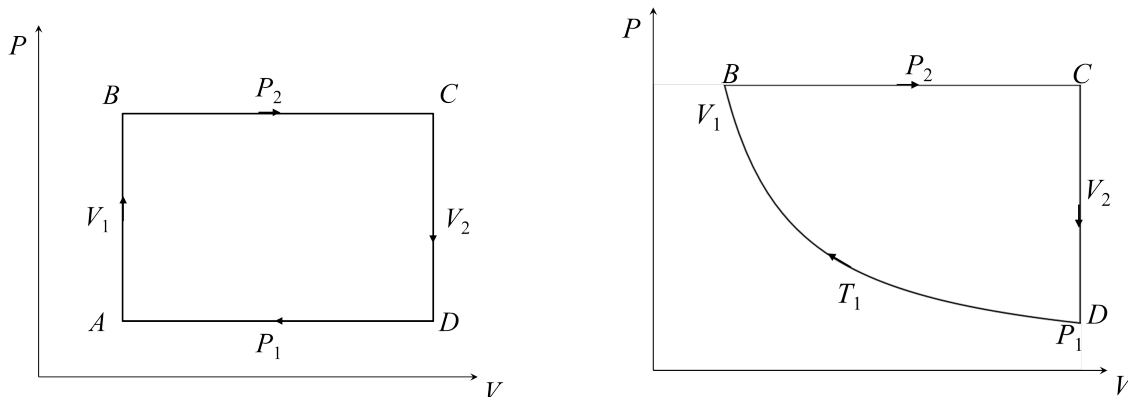

Figure 1: Isobar-isochore cycle (left) and iIsobar-isochore-isotherm cycle (right).

temperature is changing while the work is zero, thus $\delta Q = dU = \left(\frac{\partial U}{\partial T}\right)_V dT = C_V dT$. Integration for the perfect gas $C_V = $ constant proceeds as follows $S(V_0, T) = S_0 + \int_{T_0}^{T} \frac{C_V dT}{T} = S_0 + C_V \ln \frac{T}{T_0}$. During the second stage $T = $ constant. As for the ideal gas, the internal energy, $U = U(T)$, does not change and $\delta Q = PdV$. Using the equation of state of the ideal gas $PV = nRT$ this can be rewritten as $\delta Q = nRT \frac{dV}{V}$. Now integration with $T = $ constant proceeds as follows: $S(V, T) = S(V_0, T) + nR \int_{V_0}^{V} \frac{dV}{V} = S_0 + C_V \ln \frac{T}{T_0} + nR \ln \frac{V}{V_0}$. Here the terms with T_0 and V_0 can be absorbed in the constant: $S(V, T) = C_V \ln T + nR \ln V + $ constant. Using $C_P - C_V = nR$ (Mayer's relation) and $\gamma = C_P/C_V$, you can rewrite the previous expression as $S(V, T) = C_V [\ln T + (\gamma - 1) \ln V] + $ constant $= C_V \ln TV^{\gamma-1} + $ constant. The argument of the logarithm is constant in the adiabatic process, $S = $ constant. The result therefore has an expected behavior and passes an error check.

3. Express the energy of a perfect gas in the natural variables, $U = U(S, V)$, and check the relations:

$$T = \left(\frac{\partial U}{\partial S}\right)_V, \qquad -P = \left(\frac{\partial U}{\partial V}\right)_S, \qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V.$$

Solution: In the V, T variables the energy of a perfect gas has the form $U = C_V T$, where a constant has been dropped for simplicity. The entropy of the perfect gas is given by $S = C_V \ln TV^{\gamma-1}$, where again a constant has been dropped. From here you can express T as a function of S, namely $T = V^{1-\gamma} e^{S/C_V}$. Therefore the energy in its natural variables becomes $U(S, V) = C_V V^{1-\gamma} e^{S/C_V}$; note that U depends on the volume! Now, using $dU = TdS - PdV$ you can identify $T = \left(\frac{\partial U}{\partial S}\right)_V$ and $-P = \left(\frac{\partial U}{\partial V}\right)_S$. Substitute the previously obtained T relation to obtain $\left(\frac{\partial U}{\partial S}\right)_V = V^{1-\gamma} e^{S/C_V} = T$. Further, using $\gamma = C_P/C_V$ and $C_P - C_V = nR$ it follows that $\left(\frac{\partial U}{\partial V}\right)_S = -\frac{(\gamma-1)C_V}{V^\gamma} e^{S/C_V} = -\frac{nR}{V^\gamma} e^{S/C_V}$. Using again the T relation $\left(\frac{\partial U}{\partial V}\right)_S = -\frac{nRT}{V} = -P$. Thus, you have obtained $P = \frac{nR}{V^\gamma} e^{S/C_V}$, in the V, S variables. To check the Maxwell identity, use the T relation to calculate $\left(\frac{\partial T}{\partial V}\right)_S = -\frac{nR}{C_V V^\gamma} e^{S/C_V}$. On the other hand, from $P(V, S)$ it follows that $-\left(\frac{\partial P}{\partial S}\right)_V = -\frac{nR}{C_V V^\gamma} e^{S/C_V} = \left(\frac{\partial T}{\partial V}\right)_S$, as expected.

4. Express thermodynamic potentials F and G of the perfect gas in terms of their natural variables and check the relations:

$$-S = \left(\frac{\partial F}{\partial T}\right)_V, \qquad -P = \left(\frac{\partial F}{\partial V}\right)_T, \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V.$$

Solution: Use the definition of the Helmholtz potential F and the formulas for U and S of a perfect gas to obtain $F = U - TS = C_V T - TC_V \ln TV^{\gamma-1} = -C_V T \ln(TV^{\gamma-1}/e)$. Since $dF = -SdT - PdV$, you can identify $-S = \left(\frac{\partial F}{\partial T}\right)_V = -C_V + C_V + C_V \ln TV^{\gamma-1} = C_V \ln TV^{\gamma-1}$. The entropy is found to be $S = -\left(\frac{\partial F}{\partial T}\right)_V = -C_V + C_V + C_V \ln TV^{\gamma-1} = C_V \ln TV^{\gamma-1}$. The pressure is $P = -\left(\frac{\partial F}{\partial V}\right)_T = \left(\frac{\partial (C_V T \ln V^{\gamma-1})}{\partial V}\right)_T = C_V T (\gamma - 1) \left(\frac{\partial (\ln V)}{\partial V}\right)_T = \frac{C_V T (\gamma-1)}{V} = \frac{nRT}{V}$. Next,

you can verify the Maxwell relation, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$, as follows: $\left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial}{\partial V}C_V \ln TV^{\gamma-1} = C_V(\gamma-1)\frac{\partial \ln V}{\partial V} = \frac{nR}{V}$; on the other hand, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V} = \left(\frac{\partial S}{\partial V}\right)_T$, as expected. For the Gibbs thermodynamic potential G all calculations are parallel to those for F, only one has to express all the formulas via P instead of V, using the equation of state of the ideal gas.

5. The Helmholtz free energy of a certain gas has the form

$$F = -\frac{n^2 a}{V} - nRT \ln(V - nb) + J(T).$$

Find the equation of state of this gas, as well as its internal energy, entropy, heat capacities C_P and C_V and, in particular, their diference $C_P - C_V$.

Solution: To determine the equation of state, find P as a function of the native variables V, T; namely $P = -\left(\frac{\partial F}{\partial V}\right)_T = -\frac{n^2 a}{V^2} + \frac{nRT}{V-nb}$. Rearrange this expression to obtain the van der Waals equation of state of a non-ideal gas $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$. Next, the entropy is given by $S = -\left(\frac{\partial F}{\partial T}\right)_V = nR\ln(V - nb) - J'(T)$. Now the internal energy becomes $U = F + TS = -\frac{n^2 a}{V} + J(T) - TJ'(T)$. The heat capacity can be found as $C_V = \left(\frac{\partial U}{\partial T}\right)_V = -TJ''(T)$ or as $C_V = \left(\frac{\partial S}{\partial T}\right)_V = -TJ''(T)$. Finding $C_P = T\left(\frac{\partial S}{\partial T}\right)_P$ requires some algebra. The idea is simple. An explicit way to do this is to express V in the form $V = V(P,T)$ everywhere with the help of van der Waals equation of state. However, this V is a solution of a cubic equation that is better to avoid. Also this method is inconvenient to study $C_P - C_V$ because both heat capacities have to be functions of the same variables. Therefore, it is better to use the implicit method considering $S = S(V,T)$ but with $V = V(P,T)$. It follows that $C_P = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P = C_V + T\left(\frac{\partial S}{\partial V}\right)_T / \left(\frac{\partial T}{\partial V}\right)_P$. In this equation $\left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{V-nb}$, whereas $\left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{nR}\frac{\partial}{\partial V}\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = \frac{1}{nR}\left[-\frac{2n^2 a}{V^3}(V - nb) + \left(P + \frac{n^2 a}{V^2}\right)\right]$. Now, substitue the expression for $P(V,T)$ to find $\left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{nR}\left[-\frac{2n^2 a}{V^3}(V - nb) + \frac{nRT}{V-nb}\right]$. Gathering terms, you obtain $C_P - C_V = \frac{(nR)^2 T}{V-nb}\left[-\frac{2n^2 a}{V^3}(V - nb) + \frac{nRT}{V-nb}\right]^{-1}$, or equivalently $C_P - C_V = nR\frac{nRT}{nRT-(2n^2 a/V^3)(V-nb)^2}$, and finally $C_P - C_V = \frac{nR}{1-(2n^2 a(V-nb)^2)/(nRTV^3)} > nR$. It is easily seen that at high temperatures and large volumes the additional term in the denominator becomes small and Mayer's relation for the ideal gas arises.