Physics 151
Crib Sheet
2nd semester, A.Y. 2018-19

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1 P09 PS02 2.8

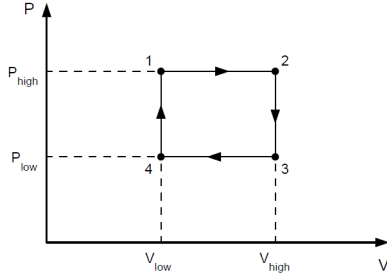Consider the cyclic process as described in Example 2.1.

Figure 1: Cyclic process for this problem.

(a) Because the system was returned to its original pressure and volume, why is the net amount of work done on the system not zero?

The net work done on the system is non-zero since it depends on the initial, intermediate, and final macrostates (i.e. the path).

(b) What would be the work done on the gas if the gas were taken from $1 \to 2 \to 3$ and then back to 1 along the diagonal path connecting 3 and 1?

$$W_{1\to2} = P_{high}(V_{high} - V_{low}) \tag{1}$$

$$W_{2\to3} = (P_{low} - P_{high})V_{high} \tag{2}$$

$$W_{3\to1} = \sqrt{P_{high}^2(V_{high} - V_{low})^2 + (P_{low} - P_{high})^2 V_{high}^2} \tag{3}$$

$$W_{net} = W_{1\to2} + W_{2\to3} + W_{3\to1} \tag{4}$$

2 P10 PS02 2.13

In Example 2.1 we showed that the net work done on the gas in the cyclic process shown in Figure 1 is nonzero. Assume that the gas is ideal with N particles and calculate the energy transfer by heating in each step of the process. Then explain why the net work done on the gas is negative and show that the net change of the internal energy is zero.

From Example 2.1, the net work done on a gas in a cyclic process was determined to be nonzero, with a value of

$$W_{net} = -(P_{high} - P_{low})(V_{high} - V_{low}) \tag{1}$$

Assuming an ideal gas with N particles, the energy transfer due to heating for each step in the process is as follows:

$$Q_{1\to2} = -Q_{3\to4} = \int_{T_1}^{T_2} c_P \, dT \tag{2}$$

$$= \nu c_P \int_{T_1}^{T_2} dT \tag{3}$$

$$= \nu c_P (T_2 - T_1) \tag{4}$$

$$= \nu c_P \Delta T \tag{5}$$

$$Q_{2\to3} = -Q_{4\to1} = \int_{T_1}^{T_2} c_V \, dT \tag{6}$$

$$= \nu c_V \int_{T_1}^{T_2} dT \tag{7}$$

$$= \nu c_V (T_2 - T_1) \tag{8}$$

$$= \nu c_V \Delta T \tag{9}$$

Recalling the ideal gas equation,

$$PV = \nu RT \tag{10}$$

$$T = \frac{PV}{\nu R} \tag{11}$$

The net energy transfer due to heating is

$$W_{net} = Q_{1\to2} + Q_{2\to3} + Q_{3\to4} + Q_{4\to1} \tag{12}$$

Plugging (11) into each of the equations in (5) and (9), we have

$$Q_{1\to2} = \nu c_P P_{high} \frac{V_{high} - V_{low}}{\nu R} \tag{13}$$

$$Q_{2\to3} = \nu c_V V_{high} \frac{P_{low} - P_{high}}{\nu R} \tag{14}$$

$$Q_{3\to4} = \nu c_P P_{low} \frac{V_{low} - V_{high}}{\nu R} \tag{15}$$

$$Q_{4\to1} = \nu c_V V_{low} \frac{P_{high} - P_{low}}{\nu R} \tag{16}$$

Simplifying equations (13) through (16) and summing them as in (12), we have

$$Q_{net} = c_P P_{high} \frac{V_{high} - V_{low}}{R}$$
$$- c_V V_{high} \frac{P_{high} - P_{low}}{R}$$
$$- c_P P_{low} \frac{V_{high} - V_{low}}{R}$$
$$+ c_V V_{low} \frac{P_{high} - P_{low}}{R} \tag{17}$$

$$Q_{net} = \frac{c_P}{R}(P_{high} - P_{low})(V_{high} - V_{low})$$
$$- \frac{c_V}{R}(P_{high} - P_{low})(V_{high} - V_{low}) \tag{18}$$

Recall that for an ideal gas,

$$c_P = \frac{5}{2}R \tag{19}$$

$$c_V = \frac{3}{2}R \tag{20}$$

Plugging these into (18),

$$Q_{net} = \frac{5}{2}R\frac{1}{R}\left(P_{high} - P_{low}\right)\left(V_{high} - V_{low}\right)$$
$$- \frac{3}{2}R\frac{1}{R}\left(P_{high} - P_{low}\right)\left(V_{high} - V_{low}\right) \tag{21}$$

Which gives us the expected relation of $Q_{net} = -W_{net}$ (negative because in a cyclic process, there is no change in internal energy; the work done is equal to the heat added):

$$Q_{net} = \left(P_{high} - P_{low}\right)\left(V_{high} - V_{low}\right) \tag{22}$$

From the first thermodynamic law,

$$\Delta E = Q + W \tag{23}$$

Plugging equations (1) and (5) into this, we have

$$\Delta E = 0 \tag{24}$$

3 P11 PS03 2.15

Use (2.44) and the ideal gas pressure equation of state in (2.8) to show that in a quasistatic adiabatic processes P and V are related as

$$PV^\gamma = \text{constant} \tag{1}$$

Also show that T and P are related as

$$TP^{(1-\gamma)/\gamma} = \text{constant} \tag{2}$$

The given equations are:

$$TV^{\gamma-1} = C \tag{3}$$

$$PV = \nu RT \tag{4}$$

Isolating T in (4),

$$T = \frac{PV}{\nu R} \tag{5}$$

Plugging this into (3),

$$\frac{PV}{\nu R}V^{\gamma-1} = C$$
$$PV^\gamma = C\nu R = C \tag{6}$$

Therefore,

$$\boxed{PV^\gamma = \text{constant}} \tag{7}$$

Similarly, isolating V from (4),

$$V = \frac{\nu RT}{P} \tag{8}$$

Plugging this into (17),

$$P\left(\frac{\nu RT}{P}\right)^\gamma = C$$
$$(\nu RT)^\gamma P^{1-\gamma} = C$$
$$T^\gamma P^{1-\gamma} = \frac{C}{(\nu R)^\gamma}$$
$$T^\gamma P^{1-\gamma} = D \tag{9}$$

Raising both sides to $1/\gamma$,

$$\left(T^\gamma P^{1-\gamma}\right)^{\frac{1}{\gamma}} = D^{\frac{1}{\gamma}}$$
$$\boxed{TP^{(1-\gamma)/\gamma} = \text{constant}} \tag{10}$$

4 P12 PS03 2.17

(a) Air initially at 20°C is compressed by a factor of 15. Assuming adiabatic conditions, $V_i/15 = V_f$, $T_i = 293$K, and $\gamma = 1.4$,

$$TV^{\gamma-1} = C \tag{1}$$
$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$
$$293 V_i^{0.4} = T_f \left(\frac{V_i}{15}\right)^{0.4}$$
$$293 = T_f \left(\frac{1}{15}\right)^{0.4}$$
$$T_f = 293 \left(\frac{1}{15}\right)^{-0.4}$$
$$\boxed{T_f = 866 \text{ K}} \tag{2}$$

Assuming air behaves like an ideal gas,

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} \tag{3}$$
$$\frac{P_i}{293}\frac{V_f}{15} = \frac{P_f V_f}{866}$$
$$\frac{P_i}{(293)(15)} = \frac{P_f}{866}$$
$$\boxed{P_i \approx 5P_f} \tag{4}$$

(b) If the compression is isothermal,

$$P_i V_i = P_f V_f \tag{5}$$
$$\boxed{P_i = 15P_f} \tag{6}$$

(c) The pressure increases more with adiabatic compression.

5 P13 PS03 2.18

(a) Use the result that we derived in (2.53) to obtain the alternative form (2.54).

From the given equations,

$$W = C_V \left(T_2 - T_1 \right) \tag{1}$$
$$PV = \nu RT \tag{2}$$
$$C_V = \frac{3}{2}\nu k_B \tag{3}$$

Plugin (15) and (3) into (1):

$$W = \frac{3}{2}\nu k_B \left(\frac{P_2 V_2}{\nu k_B} - \frac{P_1 V_1}{\nu k_B} \right)$$
$$= \frac{3}{2} \left(P_2 V_2 - P_1 V_1 \right) \tag{4}$$

Since $\gamma = \frac{5}{3}$ for monatomic ideal gas,

$$W = \frac{\left(P_2 V_2 - P_1 V_1 \right)}{\frac{2}{3}}$$
$$= \frac{\left(P_2 V_2 - P_1 V_1 \right)}{\frac{5}{3} - \frac{3}{3}}$$
$$\boxed{W = \frac{\left(P_2 V_2 - P_1 V_1 \right)}{\gamma - 1}} \tag{5}$$

(b) Show that another way to derive (2.54) is to use the relations (2.14) and (2.46).

From the given equations,

$$PV^\gamma = C \tag{6}$$
$$W = -\int_{V_1}^{V_2} P(T,V) \, dV \tag{7}$$

Isolate P from (6) and plug into (7):

$$W = -\int_{V_1}^{V_2} CV^{-\gamma} \, dV$$
$$= -C \frac{V^{1-\gamma}}{1-\gamma}\bigg|_{V_1}^{V_2}$$
$$= \frac{1}{\gamma - 1} \left(CV_2^{1-\gamma} - CV_1^{1-\gamma} \right)$$
$$= \frac{1}{\gamma - 1} \left(CV_2^{-\gamma}V_2 - CV_1^{-\gamma}V_1 \right) \tag{8}$$

From (6),

$$P = CV^{-\gamma} \tag{9}$$

Therefore,

$$\boxed{W = \frac{1}{\gamma - 1} \left(P_2 V_2 - P_1 V_1 \right)} \tag{10}$$

6 P14 PS03 2.20

A heat pump works on the same principle as a refrigerator, but the goal is to heat a room by cooling its cooler surroundings. For example, we could heat a building by cooling a nearby body of water. If we extract energy Q_{cold} from the surroundings at T_{cold}, do work W, and deliver Q_{hot} to the room at T_{hot}, the coefficient of performance is given by

$$\text{COP} = \frac{\text{what you get}}{\text{what you pay for}} = \frac{Q_{hot}}{W} \tag{1}$$

What is the maximum value of COP for a heat pump in terms of T_{cold} and T_{hot}? What is the COP when the outside temperature is $0°$C and the interior temperature is $23°$C? Is it more effective to operate a heat pump during the winters in New England where the winters are cold or in the Pacific Northwest where the winters are relatively mild? (It is too bad that the maximum efficiency of a heat pump occurs when it is needed least.)

Since we want to heat a room surrounded by a cooler environment, the work done is positive:

$$\text{COP} = \frac{Q_{hot}}{Q_{hot} - Q_{cold}} \tag{2}$$
$$= \frac{Nk_B T_{hot} \ln\left(\frac{V_f}{V_i}\right)}{Nk_B T_{hot} \ln\left(\frac{V_f}{V_i}\right) - Nk_B T_{cold} \ln\left(\frac{V_f}{V_i}\right)}$$
$$\boxed{\text{COP} = \frac{T_{hot}}{T_{hot} - T_{cold}}} \tag{3}$$

Plugging the given conditions $T_{hot} = 296$K and $T_{cold} = 273$K into (17),

$$\text{COP} = \frac{296}{296 - 273}$$
$$\boxed{\text{COP} = 12.9} \tag{4}$$

The denominator is larger for large temperature differences. The heater is more efficient in regions with mild winters.

7 P15 PS03 2.21

The temperature of 1 kg of water at $0°$C is increased to $50°$C by first bringing it into contact with a heat bath at $25°$C and then with a heat bath at $50°$C. What is the change in entropy of the entire system? How does this change in entropy compare with the change that was found in Example 2.15?

For the first bath,

$$\Delta S_{11} = C \ln \left(\frac{T_b}{T_a} \right) \tag{1}$$

$$= 4184 \ln \left(\frac{298}{273} \right)$$

$$= 366.6 \text{ J/K} \tag{2}$$

The energy transfer is

$$Q = C \left(T_b - T_a \right) \tag{3}$$

$$= 4184(25)$$

$$= 104600 \text{ J} \tag{4}$$

So the entropy of the first bath is

$$\Delta S_{12} = -\frac{Q}{T_b} \tag{5}$$

$$= -\frac{104600}{298}$$

$$= -351 \text{ J/K} \tag{6}$$

The total entropy change for the first bath is

$$\Delta S_1 = 366.6 - 351 \tag{7}$$

$$= 15.6 \text{ J/K} \tag{8}$$

Similarly, for the second bath,

$$\Delta S_{21} = 4184 \ln \left(\frac{323}{298} \right) \tag{9}$$

$$= 337.1 \text{ J/K} \tag{10}$$

$$\Delta S_{22} = -\frac{Q}{T_b} \tag{11}$$

$$= -\frac{104600}{323} \tag{12}$$

$$= -323.8 \text{ J/K} \tag{13}$$

$$\Delta S_2 = 337.1 - 323.8 \tag{14}$$

$$= 13.3 \text{ J/K} \tag{15}$$

The total entropy change for both processes is then

$$\Delta S = 15.6 + 13.3 \tag{16}$$

$$\boxed{\Delta S = 28.9 \text{ J/K}} \tag{17}$$

The value obtained is less than that of the water directly placed in contact with the 50° bath.

8   P16 PS04 2.23

(a) Show that the work performed by the heat engine in Example 2.19 is given by

$$W = C_A \left(T_A - T \right) + C_B \left(T_B - T \right) \tag{1}$$

where C_A and C_B are constants and T is given by (2.109) if the process is reversible. (Recall that our convention is to consider the work done on a system, except when we are discussing heat engines.)

Given

$$T = T_A^{\frac{C_A}{C_A + C_B}} T_B^{\frac{C_B}{C_A + C_B}} \tag{2}$$

The work done by an engine on bath A for the entire process is

$$W = -P \, dV \tag{3}$$

From the ideal gas law,

$$PV = NkT \tag{4}$$

$$d(PV) = d(NkT) \tag{5}$$

$$P \, dV = Nk \, dT \tag{6}$$

the temperature of bath A, from T_A, approaches the equilibrium temperature T. Express dV as

$$dV = \frac{Nk_B \, dT}{P} \tag{7}$$

Plugging this into (3),

$$W = -P \frac{Nk_B \, dT}{P}$$

$$= -Nk_B \, dT$$

$$= -Nk_B \left(T - T_A \right)$$

$$= Nk_B \left(T_A - T \right) \tag{8}$$

Define $C_A = N_A k_B$ as a constant inherent to bath A. The work done on bath A is

$$W_A = C_A \left(T_A - T \right) \tag{9}$$

Since the engine also does work on bath B, we can similarly define a constant inherent to bath B as $C_B = N_B k_B$. Consequently,

$$W_B = C_B \left(T_B - T \right) \tag{10}$$

Thus, the total work done by the engine is

$$W = W_A + W_B \tag{11}$$

$$\boxed{W = C_A \left(T_A - T \right) + C_B \left(T_B - T \right)} \tag{12}$$

(b) Suppose that $C_A = C_B = C$ (a constant independent of T) in (2.93) and (2.109). Compare the form of the expressions for the final temperature.

(2) becomes,

$$T = T_A^{\frac{C}{2C}} T_B^{\frac{C}{2C}}$$
$$= T_A^{\frac{1}{2}} T_B^{\frac{1}{2}}$$
$$\boxed{T = (T_A T_B)^{\frac{1}{2}}} \qquad (13)$$

Thus, the final temperature for heat engine is the square root of the product of the two initial temperatures. For GT(2.94),

$$T = \frac{CT_A + CT_B}{2C}$$
$$\boxed{T = \frac{T_A + T_B}{2}} \qquad (14)$$

The final temperature for thermal contact is the mean of the initial temperatures.

(c) Suppose that $T_A = 256$K and $T_B = 144$K. What are the relative values of the final temperatures in (2.93) and (2.109) assuming that the heat capacities of the two bodies are equal? For which process is the final temperature lower? Why?

We have $T_A = 256$ K and $T_B = 144$ K. For the heat engine, the final temperature using (13) is

$$\boxed{T = 192\text{K}} \qquad (15)$$

while for thermal contact, using (14),

$$\boxed{T = 200\text{K}} \qquad (16)$$

The final temperature for thermal contact is higher because energy from both systems contributed directly to the final temperature. The final temperature with an engine is lower because it converts some of the energy into work.

(d) Suppose that the heat capacities of both bodies depend linearly on the temperature T rather than being constant; that is, $C_A = AT$ and $C_B = BT$, where A and B are constants. What is the final temperature assuming that the two bodies are placed in thermal contact? What is the final temperature for the case when the maximum work is extracted? What is the maximum work done?

9   P17 PS04 2.24

(a) Use (2.133) to derive the relation (2.44) between T and V for a quasistatic adiabatic process.

From the given

$$\Delta S = \frac{3}{2} Nk \ln\left(\frac{T_2}{T_1}\right) + Nk \ln\left(\frac{V_2}{V_1}\right) \qquad (1)$$

The change in entropy is zero for a quasistatic adiabatic process:

$$0 = \frac{3}{2} Nk \ln\left(\frac{T_2}{T_1}\right) + Nk \ln\left(\frac{V_2}{V_1}\right) \qquad (2)$$

$$\frac{3}{2} Nk \ln\left(\frac{T_2}{T_1}\right) = -Nk \ln\left(\frac{V_2}{V_1}\right) \qquad (3)$$

$$Nk \ln\left(\frac{T_2}{T_1}\right) = -\frac{2}{3} Nk \ln\left(\frac{V_2}{V_1}\right) \qquad (4)$$

$$\ln\left(\frac{T_2}{T_1}\right) = -\frac{2}{3} \ln\left(\frac{V_2}{V_1}\right) \qquad (5)$$

Recall that for a monatomic ideal gas, $\gamma = \frac{5}{3}$. Expressing the constant coefficient on the RHS of (5) in terms of γ,

$$\gamma - 1 = \frac{5}{3} - 1 = \frac{2}{3} \qquad (6)$$

Plugging this into (5),

$$\ln\left(\frac{T_2}{T_1}\right) = -(\gamma - 1) \ln\left(\frac{V_2}{V_1}\right) \qquad (7)$$

By the power rule of exponentials,

$$\ln\left(\frac{T_2}{T_1}\right) = -\ln\left[\left(\frac{V_2}{V_1}\right)^{(\gamma-1)}\right] \qquad (8)$$

$$\ln\left(\frac{T_2}{T_1}\right) = \ln\left[\left(\frac{V_1}{V_2}\right)^{(\gamma-1)}\right] \qquad (9)$$

$$\left(\frac{T_2}{T_1}\right) = \left[\left(\frac{V_1}{V_2}\right)^{(\gamma-1)}\right] \qquad (10)$$

$$\frac{T_2}{T_1} = \frac{V_1^{\gamma-1}}{V_2^{\gamma-1}} \qquad (11)$$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \qquad (12)$$

Thus,

$$\boxed{TV^{\gamma-1} = C} \qquad (13)$$

(b) An ideal gas of N particles is confined to a box of chamber V_1 at temperature T . The gas is then allowed to expand freely into a vacuum to fill the

entire container of volume V_2. The container is thermally insulated. What is the change in entropy of the gas?

If the container is thermally insulated, $T_1 = T_2 = T$, and (5) becomes

$$\Delta S = \frac{3}{2}Nk \ln\left(\frac{T}{T}\right) + Nk \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = \frac{3}{2}Nk \ln(1) + Nk \ln\left(\frac{V_2}{V_1}\right)$$

$$\boxed{\Delta S = Nk \ln\left(\frac{V_2}{V_1}\right)} \tag{14}$$

(c) Find $\Delta S(T, P)$ for an ideal classical gas.

From the ideal gas law,

$$PV = NkT \tag{15}$$

$$V = \frac{NkT}{P} \tag{16}$$

Plugging this into (5),

$$\Delta S = \frac{3}{2}Nk \ln\left(\frac{T_2}{T_1}\right) + Nk \ln\left(\frac{\frac{NkT_2}{P_2}}{\frac{NkT_1}{P_1}}\right)$$

$$= \frac{3}{2}Nk \ln\left(\frac{T_2}{T_1}\right) + Nk \ln\left(\frac{T_2 P_1}{T_1 P_2}\right)$$

$$= \frac{3}{2}Nk \ln\left(\frac{T_2}{T_1}\right) + Nk \ln\left(\frac{T_2}{T_1}\right)$$

$$\qquad + Nk \ln\left(\frac{P_1}{P_2}\right)$$

$$= \frac{5}{2}Nk \ln\left(\frac{T_2}{T_1}\right) + Nk \ln\left(\frac{P_1}{P_2}\right)$$

$$\boxed{\Delta S(T, P) = \frac{5}{2}Nk \ln\left(\frac{T_2}{T_1}\right) + Nk \ln\left(\frac{P_1}{P_2}\right)} \tag{17}$$

10   P18 PS04 2.26

(a) Show that if the change in volume of the system is zero, $\Delta V = 0$, and the initial and final temperatures are that of the heat bath, then the maximum useful work is $-\Delta F$.

The useful work is defined as

$$W_{useful} = -\left(\Delta E + P\Delta V - T_{bath}\Delta S\right) \tag{1}$$

If $\Delta V = 0$,

$$W_{useful} = -\left(\Delta E - T_{bath}\Delta S\right) \tag{2}$$

Recall the Helmholtz free energy:

$$F = E - TS \tag{3}$$

The availability is defined as

$$\Delta A = \Delta F = \Delta E - T_{bath}\Delta S \tag{4}$$

Substituting (4) into (2),

$$\boxed{W_{useful} = -\Delta F} \tag{5}$$

(b) Show that if the initial and final temperature and pressure are that of the bath, then the maximum useful work is $-\Delta G$.

Recall the Gibbs free energy:

$$G = E - PV + TS \tag{6}$$

Taking the delta differentials,

$$\Delta G = \Delta E - (P\Delta V + V\Delta P) + (T\Delta S + S\Delta T) \tag{7}$$

If $\Delta P = \Delta T = 0$,

$$\Delta G = \Delta E - P\Delta V + T\Delta S \tag{8}$$

Substituting (8) into (1),

$$\boxed{W_{useful} = -\Delta G} \tag{9}$$

11   P19 PS04 2.25

(a) Given the definition of the enthalpy in (2.29) show that

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}P + \mu\,\mathrm{d}N \tag{1}$$

and

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N} \tag{2}$$

$$V = \left(\frac{\partial H}{\partial P}\right)_{S,N} \tag{3}$$

$$\mu = \left(\frac{\partial H}{\partial N}\right)_{S,P} \tag{4}$$

The enthalpy is defined as

$$H = E + PV \tag{5}$$

Taking the differential,

$$\mathrm{d}H = \mathrm{d}E + P\,\mathrm{d}V + V\,\mathrm{d}P \qquad (6)$$

From the fundamental thermodynamic relation,

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V + \mu\,\mathrm{d}N \qquad (7)$$

Substituting (21) into (6),

$$\mathrm{d}H = T\,\mathrm{d}S - P\,\mathrm{d}V + P\,\mathrm{d}V + \mu\,\mathrm{d}N + V\,\mathrm{d}P$$
$$\boxed{\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}P + \mu\,\mathrm{d}N} \qquad (8)$$

Therefore, the natural variables are

$$\boxed{T = \left(\frac{\partial H}{\partial S}\right)_{P,N}} \qquad (9)$$

$$\boxed{V = \left(\frac{\partial H}{\partial P}\right)_{S,N}} \qquad (10)$$

$$\boxed{\mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}} \qquad (11)$$

(b) Show that H is a minimum for an equilibrium system at fixed entropy.

The change in entropy is defined in terms of reversible heat as $\mathrm{d}Q_{rev}/T$. Thus,

$$\mathrm{d}S = \frac{\mathrm{d}Q_{rev}}{T} \geq \frac{\mathrm{d}Q_{irrev}}{T} \qquad (12)$$

or

$$\mathrm{d}Q_{rev} \leq 0 \qquad (13)$$

First law of thermodynamics:

$$\mathrm{d}Q = \mathrm{d}E + P\,\mathrm{d}V \qquad (14)$$

From (13),

$$\mathrm{d}E + P\,\mathrm{d}V \leq T\,\mathrm{d}S \qquad (15)$$
$$\mathrm{d}E \leq T\,\mathrm{d}S - P\,\mathrm{d}V \qquad (16)$$

Recall $\mathrm{d}(PV) = P\,\mathrm{d}V + V\,\mathrm{d}P$. We have

$$\mathrm{d}(E + PV) \leq T\,\mathrm{d}S + V\,\mathrm{d}P \qquad (17)$$

Enthalpy is defined as $H = E + PV$. (17) becomes

$$\mathrm{d}H \leq T\,\mathrm{d}S + V\,\mathrm{d}P \qquad (18)$$

For a system at equilibrium, $\mathrm{d}P = 0$. With $\mathrm{d}S = 0$,

$$\boxed{\mathrm{d}H \leq 0} \quad \square \qquad (19)$$

An equilibrium system spontaneously minimizes the enthalpy.

12   P20 PS04 2.27

From the differentials of the thermodynamic potentials

$$\mathrm{d}F = -S\,\mathrm{d}T - P\,\mathrm{d}V \qquad (1)$$
$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P \qquad (2)$$
$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}P \qquad (3)$$

derive the Maxwell relations

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad (4)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad (5)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad (6)$$

Also consider a variable number of particles to derive the Maxwell relations

$$\left(\frac{\partial V}{\partial N}\right)_P = \left(\frac{\partial \mu}{\partial P}\right)_N \qquad (7)$$

$$\left(\frac{\partial \mu}{\partial V}\right)_N = -\left(\frac{\partial P}{\partial N}\right)_V \qquad (8)$$

The natural variables of (1) are

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad (9)$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \qquad (10)$$

Taking the partial derivative of (9) wrt V under constant T,

$$\left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial}{\partial V}\left[\left(\frac{\partial F}{\partial T}\right)_V\right]_T$$
$$= -\frac{\partial}{\partial T}\left[\left(\frac{\partial F}{\partial V}\right)_T\right]_V$$
$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V} \qquad (11)$$

The natural variables of (2) are

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \tag{12}$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T \tag{13}$$

Taking the partial derivative of (12) wrt P under constant T,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{\partial}{\partial P}\left[\left(\frac{\partial G}{\partial T}\right)_P\right]_T$$

$$= -\frac{\partial}{\partial T}\left[\left(\frac{\partial G}{\partial P}\right)_T\right]_P$$

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P} \tag{14}$$

The natural variables of (3) are

$$T = \left(\frac{\partial H}{\partial S}\right)_P \tag{15}$$

$$V = \left(\frac{\partial H}{\partial P}\right)_S \tag{16}$$

Taking the partial derivative of (15) wrt P under constant S,

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\partial}{\partial P}\left[\left(\frac{\partial H}{\partial S}\right)_P\right]_S$$

$$= \frac{\partial}{\partial S}\left[\left(\frac{\partial H}{\partial P}\right)_S\right]_P$$

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P} \tag{17}$$

From (3), with varying number of particles,

$$dH = T\,dS + V\,dP + \mu\,dN \tag{18}$$

Consider constant S and express in terms of natural variables,

$$dH = \left(\frac{\partial H}{\partial P}\right)_N dP + \left(\frac{\partial H}{\partial N}\right)_P dN \tag{19}$$

By Euler's reciprocity relation,

$$\frac{\partial^2 H}{\partial P \partial N} = \frac{\partial^2 H}{\partial N \partial P} \tag{20}$$

$$\boxed{\left(\frac{\partial \mu}{\partial P}\right)_N = \left(\frac{\partial V}{\partial N}\right)_P} \tag{21}$$

From FTR,

$$dE = T\,dS - P\,dV + \mu\,dN \tag{22}$$

Consider constant S and express in terms of natural variables,

$$dE = -\left(\frac{\partial E}{\partial V}\right)_N dV + \left(\frac{\partial E}{\partial N}\right)_V dN \tag{23}$$

By Euler's reciprocity relation,

$$\frac{\partial^2 E}{\partial V \partial N} = \frac{\partial^2 E}{\partial N \partial V} \tag{24}$$

$$\boxed{\left(\frac{\partial \mu}{\partial V}\right)_N = -\left(\frac{\partial P}{\partial N}\right)_V} \tag{25}$$

13   P21 PS05 2.29

Calculate $\left(\frac{\partial T}{\partial V}\right)_E$ for the van der Waals energy equation of state (2.24) and show that a free expansion results in cooling.

The Van der Waals energy equation of state is given by

$$E = \frac{3}{2}Nk_BT - N\frac{N}{V}a \tag{1}$$

The Joule coefficient is given by

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{\left(\frac{\partial E}{\partial V}\right)_T}{\left(\frac{\partial E}{\partial T}\right)_V} \tag{2}$$

Performing the necessary derivatives indicated in (2) on (1), we have

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{N\frac{N}{V^2}a}{\frac{3}{2}Nk_B}$$

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_E = -\frac{2Na}{3k_BV^2}} \tag{3}$$

The change in temperature w.r.t. volume is negative, which indicates cooling.

14   P22 PS05 2.32

(a) Calculate the Legendre transform of $f(x) = x^3$.

The Legendre transform of a function $f(x)$ is given by

$$\mathcal{G}[m(x)] = f(x) - xm \tag{1}$$

where $m = f'(x)$.

Let $f = x^3$. It's Legendre transform is

$$\mathcal{G}[m(x)] = x^3 - x(3x^2)$$

$$= -2x^3 \tag{2}$$

But this must be expressed only in terms of m. Using $m = f'(x)$,

$$m = 3x^2$$

$$x = \sqrt{\frac{m}{3}} \qquad (3)$$

Thus,

$$\boxed{\mathcal{G}\left[x^3\right] = -2\left(\frac{m}{3}\right)^{\frac{3}{2}}} \qquad (4)$$

(b) Calculate the Legendre transforms of the functions $f(x) = x$ and $f(x) = \sin x$ if they exist.

Let $f(x) = x$. Its Legendre transform is

$$\mathcal{G}[m(x)] = f(x) - xm$$
$$= x - x(1)$$
$$\boxed{\mathcal{G}[x] = 0} \qquad (5)$$

The Legendre transform for $\sin x$ does not exist (there is no one-to-one correspondence between x and m).

15 P23 PS05 2.33

Start from the function $E(S, V, N)$ and use the Legendre transform to find the function $F(T, V, N)$.

From the fundamental thermodynamic relation,

$$dE = T\, dS - P\, dV + \mu\, dN \qquad (1)$$

Applying Legendre transform on (21) to eliminate S in favor of T,

$$\mathcal{L}[E(S, V, N)]_S = E - S\frac{\partial E}{\partial S} \qquad (2)$$

From (21), we know that $\frac{\partial E}{\partial S}$ is the expression for the natural variable T. Thus we have

$$\mathcal{L}[E(S, V, N)]_S = E - TS \qquad (3)$$

We know this expression to be the Helmholtz free energy

$$F = E - TS \qquad (4)$$

Therefore,

$$\boxed{\mathcal{L}[E(S, V, N)] = F(T, V, N)} \quad \square \qquad (5)$$

16 P24 PS05 2.54

A black hole is created from the collapse of a massive object into one so dense that nothing can escape beyond a certain radius, including light. The measurable properties of a black hole depend only on its mass, charge, and angular momentum. In this problem we estimate the entropy and temperature of a charge neutral nonrotating black hole.

(a) Because the properties of the black hole depend only on its mass, use dimensional analysis to estimate the radius R of a black hole in terms of its mass M, the gravitational constant G, and the speed of light c. (Black holes are a consequence of the general theory of relativity, and thus we expect that the radius depends only on M, G, and c.)

The radius of a black hole depends on the following:

$$F_G = G\frac{M}{R^2} = \left[\frac{\text{m}^3}{\text{kg} \cdot \text{s}^2}\right]\left[\frac{\text{kg}}{\text{m}^2}\right] \qquad (1)$$

$$c = \text{constant} = \left[\frac{\text{m}}{\text{s}}\right] \qquad (2)$$

$$M = \text{constant} = [\text{kg}] \qquad (3)$$

We can estimate the radius R of the black hole by dimensional analysis of (1)-(3). We have

$$R \approx \frac{GM}{c^2} = \frac{\left[\frac{\text{m}^3}{\text{kg} \cdot \text{s}^2}\right][\text{kg}]}{\left[\frac{\text{m}}{\text{s}}\right]^2} = [\text{m}] \qquad (4)$$

Therefore, the radius of a black hole is

$$\boxed{R \approx \frac{GM}{c^2}} \qquad (5)$$

(b) Assume that the entropy is of order Nk, where N is the number of particles in the black hole. The maximum entropy occurs when the particles are photons of wavelength λ of the order of the diameter of the black hole. Take $\lambda = 2R$ and determine the entropy S as a function of M (the total energy is Mc^2 and the energy of a photon is hc/λ). More detailed theoretical arguments give the correct relation

$$S = k\frac{8\pi^2 GM^2}{hc} \qquad (6)$$

Your approximate result should have the correct dependence on G, M, h, c, and k. Calculate a numerical value for the entropy for a one solar mass black hole using (2.249). (The solar mass $M_\odot \approx 2 \times 10^{30}$ kg.)

Taking photons with wavelength λ

$$\lambda = 2R = 2\frac{GM}{c^2} \tag{7}$$

whose energy E_γ is

$$E_\gamma = \frac{hc}{\lambda} \tag{8}$$

$$= \frac{hc^3}{2GM} \tag{9}$$

and the black hole's total energy E

$$E = Mc^2 \tag{10}$$

The momentum of a photon is given by

$$p_\gamma = \frac{h}{\lambda} \tag{11}$$

If we consider the system to behave classically and non-relativistically, then we can recall the classical momentum

$$p = mv \tag{12}$$

and from this, we see that we can divide (11) by the photon's velocity c to get its mass

$$m_\gamma = \frac{h}{c\lambda} \tag{13}$$

If we assume that the entropy of the black hole is of order Nk, where N is the number of particles in the black hole, and that all the particles are photons, we can estimate this entropy to be

$$S \approx Nk_B \tag{14}$$

where k_B is Boltzmann's constant. If the total energy of the black hole is given by (10), the number of photons is

$$N = \frac{E}{E_\gamma} = \frac{2GM^2}{hc} \tag{15}$$

Plugging this into (14),

$$\boxed{S = k_B \frac{2GM^2}{hc}} \tag{16}$$

The entropy for a black hole of one solar mass is $\boxed{S \approx 4 \times 10^{52} \text{ J} \cdot \text{K}}$.

(c) Express the entropy in terms of the surface area A of the black hole instead of M. Note that the area is a direct measure of the entropy. Does the entropy increase or decrease when two black holes coalesce into one?

Recall the surface area of a sphere:

$$A = 4\pi R^2 \tag{17}$$

Plugging in (6) into this,

$$A = \frac{4\pi M^2}{c^4} \tag{18}$$

Plugging this into (16),

$$\boxed{S = k_B \frac{\pi G c^3}{2h} A} \tag{19}$$

Thus, entropy increases when black holes coalesce.

(d) Express S in terms of the total energy E instead of M and determine the temperature for a one solar mass black hole. Use the approximation for R obtained in part (a) to find the temperature in terms of the gravitational field g at the radius R.

Using (6) to express (16) in terms of E,

$$S = k_B \frac{8\pi^2 G E^2}{hc^5} \tag{20}$$

From the equation of state of S,

$$dE = T\,dS - P\,dV + \mu\,dN \tag{21}$$

we see that the natural variable T can be expressed as

$$T = \left(\frac{\partial S}{\partial E}\right)^{-1} \tag{22}$$

Performing the differentiation on (20),

$$T = \left(k_B \frac{16\pi^2 G E}{hc^5}\right)^{-1} \tag{23}$$

We express (23) once again in terms of M so that

$$\boxed{T = \frac{hc^3}{16k_B \pi^2 GM}} \tag{24}$$

So the temperature for a black hole of one solar mass is $\boxed{T \approx 5 \times 10^{-8} \text{ K}}$.

Expressing (24) in terms of R in (6),

$$\boxed{T = \frac{hc}{16k_B \pi^2 R}} \tag{25}$$

17   P25 PS05 2.57

Consider a system described by the van der Waals equation of state which expands at constant temperature from volume V_1 to volume V_2. Assume that the density $\rho = N/V \ll 1$ over the range of volumes of interest.

(a) Calculate the work W_{vdw} done on the gas to the lowest relevant order in ρ.

The Van der Waals equation of state is given by

$$\left(P + \frac{N^2}{V^2}\right)(V - Nb) = NkT \qquad (1)$$

Since the density $\rho = \frac{N}{V} \ll 1$, (1) can be approximated as

$$P(V - Nb) = NkT \qquad (2)$$

Rearranging terms to isolate P,

$$P = \frac{NkT}{V - Nb} \qquad (3)$$

The work done on the gas is

$$W = -\int_{V_1}^{V_2} P \, dV \qquad (4)$$

Plugging in (3) into (4),

$$\begin{aligned}
W_{VDW} &= -\int_{V_1}^{V_2} \frac{NkT}{V - Nb} \, dV \\
&= -NkT \int_{V_1}^{V_2} \frac{dV}{V - Nb} \qquad (5)
\end{aligned}$$

Let $u \equiv V - Nb$, $du \equiv dV$.

$$\begin{aligned}
W_{VDW} &= -NkT \int_{V_1 - Nb}^{V_2 - Nb} \frac{du}{u} \\
&= -NkT \ln(u) \Big|_{V_1 - Nb}^{V_2 - Nb} \\
&= -NkT[\ln(V_2 - Nb) - \ln(V_1 - Nb)]
\end{aligned}$$

$$\boxed{W_{VDW} = NkT \ln\left[\frac{V_1 - Nb}{V_2 - Nb}\right]} \qquad (6)$$