Supplemental Examples for *Essentials of Modern Thermodynamics*

Chapter 1: Thermodynamics Systems

No supplemental examples for this chapter.

Chapter 2: Equations of State

Example (a) The number density of interstellar gas clouds is about 10^4 molecules per milliliter. Using the ideal gas law calculate the pressure for a temperature of 10 Kelvin. (b) The NASA Space Environment Simulation Laboratory is a giant vacuum chamber that can reach pressures as low at 10^{-5} torr; for $T = 10$ K find the number density.

Solution (a) We can use the ideal gas law either in the form $pV = NRT$ or $pV = \mathcal{N}k_\mathrm{B}T$ where $\mathcal{N}$ is the number of molecules. Since we're given the number density we'll use the latter with $\mathcal{N} = 10^4$ and $V = 1$ mL $= 10^{-6}$ m^3. If you prefer to work with moles then you just convert using $N = \mathcal{N}/\mathrm{N_A}$ where $\mathrm{N_A} = 6.023 \times 10^{23}$ mol^{-1} is Avogadro's number.

Since Boltzmann's constant is $k_\mathrm{B} = 1.38 \times 10^{-23}$ J/K and the temperature is $T = 10$ K we have $p = \mathcal{N}k_\mathrm{B}T/V = 1.38 \times 10^{-12}$ Pa, which is roughly 10^{-17} atmospheres. The point of this problem is that you need to be careful with units.

(b) The pressure is $p = 10^{-5}$ torr $= 1.3$ mPa so the number density is

$$n = \frac{\mathcal{N}}{V} = \frac{p}{k_\mathrm{B}T} \approx 10^{19} \text{ molecules/m}^3$$

Example Consider a heterogeneous isolated system consisting of a pair of closed containers separated by a solid conductive wall (i.e., the containers can exchange energy but not mass). The containers are rigid (i.e., constant volumes). Container A has two kg of helium gas and there are four kg of the helium gas in container B. Initially the total kinetic energy of the gas molecules in A is exactly equal to the total kinetic energy of the gas molecules in B. Consider the helium to be an ideal gas with all the internal energy being kinetic energy (i.e., negligible inter-molecular potential energy). Assume a quasi-static process, that is, each container remains close to an equilibrium state in time.

(a) Sketch a graph of the temperatures, $T_A(t)$, and $T_B(t)$, as a function of time t. What are the values of $T_A(t)/T_A(0)$ and $T_A(t)/T_B(t)$ in the limit $t \to \infty$?

(b) Sketch a graph of the internal energies, $U_A(t)$, and $U_B(t)$, as a function of time t. What are the values of $U_A(t)/U_A(0)$ and $U_A(t)/U_B(t)$ in the limit $t \to \infty$?

(c) Sketch a graph of the pressures, $p_A(t)$, and $p_B(t)$, as a function of time t. What are the values of $p_A(t)/p_A(0)$ and $p_A(t)/p_B(t)$ in the limit $t \to \infty$?

Solution (a) Given that initially $U_A = U_B$ and $M_A = \frac{1}{2}M_B$ then using $U = c_V M T$ we know that initially $T_A = 2T_B$. The total system reaches equilibrium when the temperatures are equal and energy is conserved so $U_A + U_B = c_V(M_A + M_B)T_\mathrm{eq}$ or

$$T_\mathrm{eq} = \frac{2U_A(0)}{c_V(3M_A)} = \frac{2}{3}T_A(0)$$

Thus $T_A(t) \to \frac{2}{3}T_A(0)$ and $T_B(t) \to \frac{4}{3}T_B(0)$. Figure 1 has the sketches for T, U, and p.
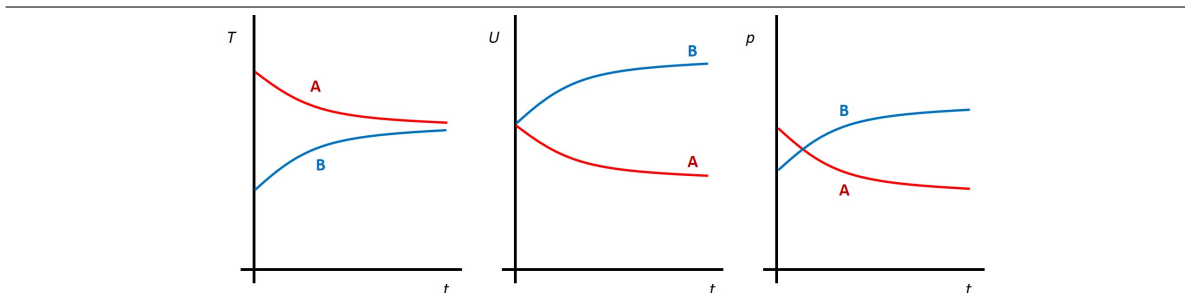
Figure 1: Temperature, internal energy, and pressure as functions of time.

(b) Since $U_A(0) = c_V M_A T_A(0)$ and $T_{\text{eq}} = \frac{2}{3}T_A(0)$ then $U_A(t) \to \frac{2}{3}U_A(0)$ as $t \to \infty$; by energy conservation $U_B(t) \to \frac{4}{3}U_B(0)$.

(c) By the ideal gas law $p(t) = (N\mathrm{R}/V)T(t)$ so the results for pressure are the same as for temperature with a multiplicative constant, $N\mathrm{R}/V$. This means that $p_A(t) \to \frac{2}{3}p_A(0)$ and $p_A(t)/p_B(t) \to V_B/V_A$. Note that the graph is *not* the same as in (a) since we know nothing about the volumes V_A and V_B except that they're constant. Because the containers are rigid $p_A \neq p_B$ at equilibrium; these pressures depend on the volume of each container.

Example The ideal gas law is only accurate for dilute gases. A more accurate model is the van der Waals equation,

$$p = \frac{N\mathrm{R}T}{V - Nb} - a\left(\frac{N}{V}\right)^2$$

The van der Waals coefficients, a and b, may be found on-line (`https://en.wikipedia.org/wiki/Van_der_Waals_constants_(data_page)`).

(a) A 10 liter vessel contains 100 moles of molecular nitrogen gas at a temperature of 300 Kelvin. Calculate the pressure using the ideal gas equation and using the van der Waals equation; find the percent difference between the two results.

(b) Plot the pressure p versus the number of moles for N between zero and 100; take $V = 10$ liters and $T = 300$ K. Make one graph with two curves, one for the ideal gas equation and one for the van der Waals equation.

Solution (a) From the ideal gas law, $p = N\mathrm{R}T/V = 246$ atmospheres. From Wikipedia, the coefficients for nitrogen are $a = 1.370$ L^2 atm/mol^2 and $b = 0.0387$ L/mol. From the van der Waals equation,

$$p = \frac{N\mathrm{R}T}{V - Nb} - a\left(\frac{N}{V}\right)^2 = 264 \text{ atm}$$

The difference is about 7%.

(b) The graph is shown in Figure 2. Notice that at low densities (small N) the van der Waals pressure is slightly lower than the ideal gas law pressure due to the attraction term (the "a" coefficient) while at high density the van der Waals pressure is higher than the ideal gas law due to the repulsion term (the "b" coefficient).

Example Equations of state are often expressed in terms of the *molar volume*, $v = V/N$, which is an intensive variable.

(a) Write the van der Waals equation of state as $p(T, v)$.

(b) Formulate your result from part (a) as a power series in $1/v$ up to third order. That is, write it as

$$p(T, v) = \frac{f_1(T)}{v} + \frac{f_2(T)}{v^2} + \frac{f_3(T)}{v^3} + \dots$$

and find the functions f_1, f_2, and f_3. Hint: Use a Taylor expansion $(1 - x)^{-1} = 1 + x + x^2 + \dots$.

(c) Use your result from part (b) to find the Boyle temperature, T_{B}, which is defined as the temperature at which, to leading order, the pressure equals that of an ideal gas (i.e., $p(T_{\mathrm{B}}, v) = \mathrm{R}T_{\mathrm{B}}/v + O(1/v^3)$).

Solution (a) By inspection the van der Waals equation may be written as,

$$p(T, v) = \frac{\mathrm{R}T}{v - b} - \frac{a}{v^2}$$

(b) The second term on the right hand side (the attraction term) is already in the desired form so we only have to treat the first term. We write the denominator for that term as,

$$\frac{1}{v - b} = \frac{1}{v}\left(1 - \frac{b}{v}\right)^{-1} = \frac{1}{v}\left(1 + \frac{b}{v} + \frac{b^2}{v^2} + \dots\right)$$

using the Taylor expansion $(1 - x)^{-1} = 1 + x + x^2 + \dots$. Putting it all together,

$$\begin{aligned} p &= \frac{\mathrm{R}T}{v}\left(1 + \frac{b}{v} + \frac{b^2}{v^2} + \dots\right) - \frac{a}{v^2} \\ &= \frac{\mathrm{R}T}{v} + \frac{\mathrm{R}Tb - a}{v^2} + \frac{\mathrm{R}Tb^2}{v^3} + \dots \end{aligned}$$

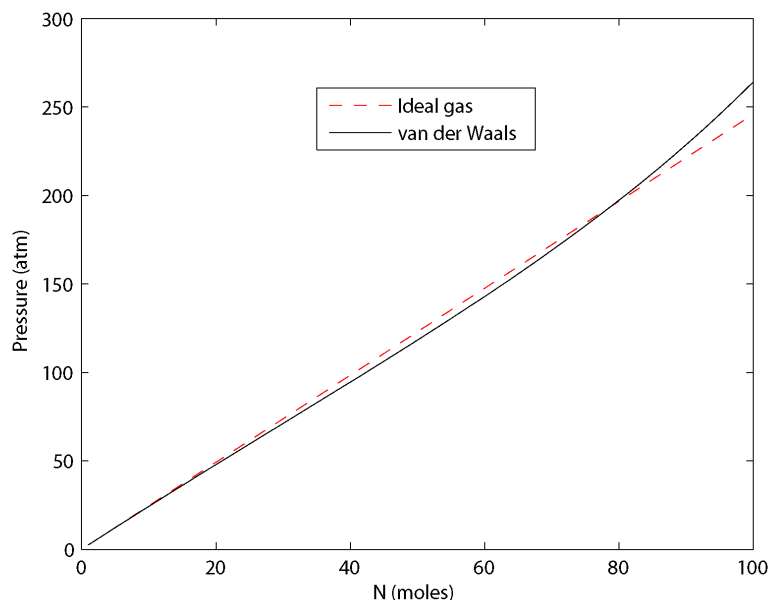
Figure 2: Pressure versus density for ideal gas (dashed line) and van der Waals (solid line).

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(c) The second term in the series vanishes when $\mathrm{R}Tb = a$ so the Boyle temperature is $T_\mathrm{B} = a/b\mathrm{R}$.

Example The free electrons in a metal can be treated as a quantum gas with the equation of state being approximated as
$$p = \frac{2}{5}\frac{N\mathrm{R}T_\mathrm{F}}{V}$$
where T_F is Fermi temperature. This approximation is accurate when $T \ll T_\mathrm{F}$.

(a) Find the number of moles of free electrons in one cubic centimeter of iron, assuming 2 free electrons per atom. Use Wikipedia to find any needed data for iron; assume room temperature.

(b) The Fermi temperature of iron is 130000 Kelvin. Find the pressure (in atmospheres) of the free electrons in iron.

Solution (a) From Wikipedia, the standard atomic weight of iron is 55.84 grams per mole. The mass density at room temperature is 7.87 grams per cubic centimeter, which gives 0.141 moles of iron atoms per cubic centimeter. Since there are two free electrons per atom this makes $N/V = 0.282$ mol/cm^3.

(b) Taking $N = 0.282$ moles, $V = 1$ cm$^3 = 10^{-6}$ m^3, then $p = 122 \times 10^9$ Pascals or about 1.2 million atmospheres. Note that it's the enormous pressure in a free electron gas that supports a white dwarf star against gravitational collapse.

Chapter 3: Work and the First Law

Example Consider the infinitesimal quantity,

$$dF = (x^2 - y)dx + xdy$$

(a) Show that dF is not an exact differential.
Hint: See `https://en.wikipedia.org/wiki/Exact_differential`
   (b) Evaluate the integral $\int dF$ between the points $(x, y) = (1, 1)$ and $(2, 2)$ for the following three paths consisting of straight-line segments:

$$(1, 1) \rightarrow (1, 2) \rightarrow (2, 2)$$
$$(1, 1) \rightarrow (2, 1) \rightarrow (2, 2)$$
$$(1, 1) \rightarrow (2, 2)$$

   (c) Consider the infinitesimal quantity,

$$dG = \frac{dF}{x^2} = (1 - y/x^2)dx + (1/x)dy$$

Show that dG is an exact differential.
   (d) Evaluate the integral $\int dG$ between the points $(x, y) = (1, 1)$ and $(2, 2)$ for the three paths defined in part (b).

   Solution (a) If dF is an exact differential then

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy$$

and by one of the identities for partial derivatives,

$$\left(\frac{\partial}{\partial y}\right)_x \left(\frac{\partial F}{\partial x}\right)_y = \left(\frac{\partial}{\partial x}\right)_y \left(\frac{\partial F}{\partial y}\right)_x$$

However,

$$\left(\frac{\partial}{\partial y}\right)_x (x^2 - y) = -1$$
$$\left(\frac{\partial}{\partial x}\right)_y x = +1$$

Since these are not equal then dF is not an exact differential.
   (b) The integral for the first path is,

$$
\begin{aligned}
\int dF &= \left[\int_1^2 xdy\right]_{x=1} + \left[\int_1^2 (x^2 - y)dx\right]_{y=2} \\
&= \int_1^2 dy + \int_1^2 (x^2 - 2)dx \\
&= (1) + (1/3) = 4/3
\end{aligned}
$$

Similarly, for the second path,

$$\int dF = \left[\int_1^2 (x^2 - y)dx\right]_{y=1} + \left[\int_1^2 xdy\right]_{x=2} = 10/3$$

The last path is along the line $x = y$ so $dx = dy$,

$$\int dF = \int_1^2 (x^2 - x)dx + \int_1^2 xdx = 7/3$$

Since dF is not an exact differential it's not surprising that each path gives a different result.

(c) Repeating a calculation similar to part (a) we have,

$$\left(\frac{\partial}{\partial y}\right)_x (1 - y/x^2) = -1/x^2$$

$$\left(\frac{\partial}{\partial x}\right)_y 1/x = -1/x^2$$

Since these are are equal then dG is an exact differential.

(d) The procedure is the same as in part (b). For the first path,

$$\int dG = \left[\int_1^2 1/xdy\right]_{x=1} + \left[\int_1^2 (1 - y/x^2)dx\right]_{y=2} = (1) + (0) = 1$$

For the second path,

$$\int dG = \left[\int_1^2 (1 - y/x^2)dx\right]_{y=1} + \left[\int_1^2 1/xdy\right]_{x=2} = (1/2) + (1/2) = 1$$

Finally, for the third path,

$$\int dG = \int_1^2 (1 - 1/x)dx + \int_1^2 1/xdx = (1 - \ln 2) + (\ln 2) = 1$$

Example One mole of a monatomic ideal gas ($C_V = \frac{3}{2}RN$) undergoes a cyclic process that is an ellipse in the $p - V$ diagram. The path goes clockwise with the pressures and volumes at the four axis points of the ellipse being:

$$p_A = 2 \times 10^5 \text{ Pa}, \quad V_A = 1 \text{ liter} \qquad p_B = 3 \times 10^5 \text{ Pa}, \quad V_B = 2 \text{ liter}$$
$$p_C = 2 \times 10^5 \text{ Pa}, \quad V_C = 3 \text{ liter} \qquad p_D = 1 \times 10^5 \text{ Pa}, \quad V_D = 2 \text{ liter}$$

(a) Find the work done on this system per cycle. (b) Find the change in the internal energy going from point A to point C, that is, $\Delta U_{AC} = U_C - U_A$. (c) Find the heat absorbed by the gas going from point A to point C, that is, $Q_{AC} = \int dQ$ along the path that is the upper half of the ellipse.

Solution (a) The area of an ellipse of width w and height h is $\frac{1}{4}\pi wh$. The work done on the system is

$$W_{\circlearrowright} = -\oint p(V) \; dV = -\frac{1}{4}\pi(V_C - V_A)(p_B - p_D) = -\frac{1}{4}\pi(2\text{l})(2 \times 10^5\text{Pa}) = -314 \text{ J}$$

This is negative since the cycle is clockwise. Note that the work done *by* the system is $W_{\circlearrowright} = -W_{\text{cycle}} = +314$ J.

(b) To find U we first find the temperatures at the two points. Using ideal gas law we get $T_A = 24$ K and $T_C = 72$ K so $\Delta U_{AC} = C_V(T_C - T_A) = 599$ J.

(c) Using First Law we can find the heat added as $Q_{AC} = \Delta U_{AC} - W_{AC}$. The work done on the system in going from point A to point C along the elliptical path is $W_{AC} = -\int_A^C pdV$. This is just the

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area under the curve in the $p - V$ diagram and that is half the area of the ellipse plus the area under a line connecting points A and C, that is,

$$W_{\mathrm{AC}} = -\int_{\mathrm{A}}^{\mathrm{C}} pdV = \frac{1}{2}(-314 \text{ J}) - p_{\mathrm{A}}(V_{\mathrm{C}} - V_{\mathrm{A}}) = -557 \text{ J}$$

The heat added is thus $Q_{\mathrm{AC}} = (599 \text{ J}) - (-557 \text{ J}) = 1156 \text{ J}$.

Example Consider the apparatus shown in Figure 3. Two cylinders, labeled A and B, are filled with an ideal gas; the initial pressure in each cylinder is 10^4 Pascals. The cross-sectional areas of the cylinders are $A_A = 0.02 \text{ m}^2$ and $A_B = 0.01 \text{ m}^2$, respectively. The cylinders have massless pistons that are connected by massless rods; the upper stem is initially clamped so the height of each piston is $x_A^i = 0.1$ m and $x_B^i = 0.3$ m. At the top of the apparatus is a 100 Newton weight; the whole apparatus is inside a vacuum chamber (i.e., exterior pressure is zero) and held at constant temperature.

(a) When the clamp is released the pistons move together; show that they move *upward*, lifting the 100 Newton weight.

(b) Some time after the clamp is released the system reaches thermodynamic equilibrium. Show that the distance that the pistons move upward is $\Delta x = 0.3$ m, that is, $x^f = x^i + \Delta x$ for each piston.

(c) Find W, the total work done (in Joules) on the gas in the two cylinders between the initial and final states. Hint: Do *not* use $W = -\int pdV$.

(d) Find Q, the total heat added (in Joules) to the gas in the two cylinders between the initial and final states.
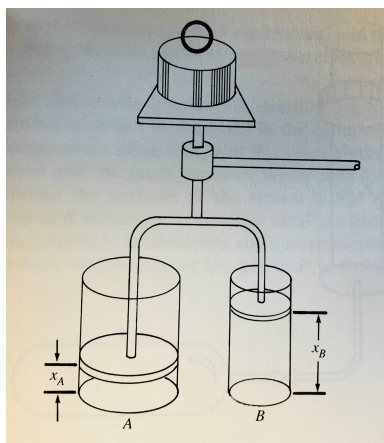
Figure 3: System with dual pistons.

Solution (a) Since $p_A^i = p_B^i = 10^4$ Pascals the upward force exerted by each piston is initially $F_A^i = p_A^i A_A = 200$ N and $F_B^i = p_B^i A_B = 100$ N. The total upward force is 300 Newtons, which exceeds to downward 100 Newton force exerted by the weight so the pistons initially move upward.

(b) At equilibrium the total upward force exerted by the gas pressure must equal the 100 Newton force exerted by the weight. That is,

$$100 \text{ N} = p_A^f A_A + p_B^f A_B$$

Using ideal gas law ($pV = NRT$) we have $p_A^i V_A^i = p_A^f V_A^f$ since N and T are constant. With this,

$$100 \text{ N} = \left(\frac{p_A^i V_A^i}{V_A^f} \right) A_A + \left(\frac{p_B^i V_B^i}{V_B^f} \right) A_B$$

$$= \frac{20 \text{ Joules}}{V_A^f / A_A} + \frac{30 \text{ Joules}}{V_B^f / A_B} = \frac{20 \text{ Joules}}{0.1 \text{ m} + \Delta x} + \frac{30 \text{ Joules}}{0.3 \text{ m} + \Delta x}$$

since $V^i = A x^i$ and $V^f = A x^f = A(x^i + \Delta x)$. After some algebra you can solve this as a quadratic equation for Δx or just verify by substitution that $\Delta x = 0.3$ m.

(c) By the work-energy theorem the work done *by* the gas in lifting the weight equals the change in gravitational potential energy so $\mathcal{W} = (100 \text{ N})(0.3 \text{ m}) = 30$ Joules. The work done *on* the gas is $W = -\mathcal{W} = -30$ Joules.

(d) For an ideal gas the internal energy is only a function of temperature so $\Delta U = 0$ for an isothermal expansion. By the First Law then $W + Q = 0$ or $Q = -W = +30$ Joules.

Chapter 4: Heat and the First Law

Example A system consists of an ideal gas initially at temperature $T_i = 300$ K, volume $V_i = 2.0$ L, and pressure $p = 1.0$ bar. (a) Find the number of moles, N. (b) If the system is expanded isothermally to a final volume of $V_f = 4.0$ L then find the final pressure, p_f. (c) If the system is expanded adiabatically to a final volume of $V_f = 4.0$ L then find the final pressure, p_f and the final temperature, T_f. Assume that $C_V = \frac{3}{2}RN$.

Solution (a) From ideal gas law, $N = p_i V_i / RT_i = 0.0801$ moles. (b) Since temperature is fixed the pressure is $p_f = NRT_i/V_f = p_i V_i/V_f = 0.5$ bars. (c) Since $C_V = 3NR/2$ then $C_p = 5NR/2$ and $\gamma = C_p/C_V = 5/3$. For an adiabatic expansion,

$$p_f V_f^\gamma = p_i V_i^\gamma$$

so

$$p_f = p_i (V_i/V_f)^\gamma = (1 \text{ bar})(1/2)^{5/3} = 0.315 \text{ bar}$$

To get the final temperature we can use the expression for adiabatic expansions or just plug the final pressure into the ideal gas law, $T_f = p_f V_f / NR = 189$ K.

Example The equation of state for pressure in hard sphere gas is

$$p = \frac{NRT}{V - bN}$$

where b is a positive constant and $V > bN$. Note that this is the van der Waals equation with $a = 0$. As with an ideal gas, for the hard sphere gas the internal energy only depends on the temperature so we assume $U = C_V T$; we also have that $C_p - C_V = NR$.

(a) Show that for a closed system ($dN = 0$),

$$dQ = C_V dT + p dV \qquad \text{and} \qquad dQ = C_p dT - (V - bN) dp$$

(b) Using the result from part (a) show that when N moles of a hard sphere gas, initially at pressure p_0, volume V_0 and temperature T_0, undergoes an adiabatic process then,

$$p = p_0 \frac{(V_0 - bN)^\alpha}{(V - bN)^\alpha} \qquad \text{and} \qquad T = T_0 \frac{(V_0 - bN)^\beta}{(V - bN)^\beta}$$

where α and β are constants that may be written in terms of $\gamma = C_p/C_V$.

Solution (a) This problem is very similar to the derivation for an ideal gas. We can start with the First Law,

$$dQ = dU + p dV$$

As with an ideal gas, $U = C_V T$ so $dU = C_V dT$ and thus

$$dQ = C_V dT + p dV \qquad (*)$$

Using the hard sphere gas law, $pV' = NRT$, where $V' = V - bN$; note that $dV' = dV$ since b and N are constant. So for an infinitesimal process we have

$$d(pV') = d(NRT)$$

Since N is fixed and R is a constant,

$$pdV' + V'dp = NR(dT)$$

so

$$
\begin{aligned}
dQ &= C_V dT + (NkdT - V'dp) \\
&= (C_V + Nk)dT - V'dp = C_p dT - V'dp \qquad (**)
\end{aligned}
$$

(b) For an adiabatic process ($dQ = 0$), we may write $(*)$ and $(**)$ as,

$$pdV = -C_V dT \qquad \text{and} \qquad V'dp = C_p dT$$

Dividing the latter equation by the former,

$$\frac{dp}{p} = -\frac{C_p}{C_V}\frac{dV}{V'} = -\gamma \frac{dV'}{V'}$$

Integrate both sides and you get,

$$\ln p = -\gamma \ln V' + a$$

where a is the constant of integration. From this we have

$$p = A(V - bN)^{-\gamma}$$

where $A = e^a$ is a constant. This constant may be fixed by the initial state so

$$p = p_0 \frac{(V_0 - bN)^\gamma}{(V - bN)^\gamma}$$

so $\alpha = \gamma$. Finally, inserting equating the equation gives,

$$T = T_0 \frac{(V_0 - bN)^{(\gamma-1)}}{(V - bN)^{(\gamma-1)}}$$

so $\beta = \gamma - 1$. You could have guessed these results for α and β since the expressions have to match the results for a ideal gas when we set $b = 0$.

Example The van der Waals equation for the pressure in a moderately dense gas is,

$$p = \frac{NRT}{V - Nb} - a\left(\frac{N}{V}\right)^2$$

where a, b are positive constants and $V > bN$. For an ideal gas the internal energy is $U_{id} = c_v MT$; for a van der Waals gas it is $U_{vw} = U_{id} - aN^2/V$. Find $C_p - C_V$ for a van der Waals gas in terms of the coefficients a and b. Check that your answer gives $C_p - C_V = NR$ when $a = 0$.

Solution In this chapter we derive the expression,

$$C_p - C_V = \left[p + \left(\frac{\partial U}{\partial V}\right)_{T,N}\right]\left(\frac{\partial V}{\partial T}\right)_{p,N}$$

To use the given expression we need to evaluate some partial derivatives. First,

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\right)_T\left[c_V MT - a\frac{N^2}{V}\right] = a\frac{N^2}{V^2}$$

For the other derivatives it's useful to take the van der Waals equation of state,

$$\left(p + a \left(\frac{N}{V} \right)^2 \right) (V - Nb) = N\mathrm{R}T$$

and take the derivative $(\partial/\partial T)_p$ on both sides to get,

$$\left(-2a \left(\frac{N^2}{V^3} \right) \left(\frac{\partial V}{\partial T} \right)_p \right) (V - Nb) + \left(p + a \left(\frac{N}{V} \right)^2 \right) \left(\frac{\partial V}{\partial T} \right)_p = N\mathrm{R}$$

Collecting terms we have,

$$\left(\frac{\partial V}{\partial T} \right)_p = N\mathrm{R} \left(p - a\frac{N^2}{V^2}\frac{V - 2Nb}{V} \right)^{-1}$$

Finally,

$$C_p - C_V = \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_p = N\mathrm{R} \left[p + a\frac{N^2}{V^2} \right] \left(p - a\frac{N^2}{V^2}\frac{V - 2Nb}{V} \right)^{-1}$$

By inspection we get the ideal gas result of $C_p - C_V = N\mathrm{R}$ when $a = 0$.

Example Figure 4 illustrates the free expansion of a gas in a heterogeneous isolated system. Initially the system is divided into two subsystems; the left side has N moles of a pure dilute gas at initial temperature T_A and volume V_A while the right side is vacuum. The plug separating the two sides is removed and the gas is allowed to fill the entire system until it reaches thermodynamic equilibrium in a total volume V_B.

a) Find ΔU_{AB} and ΔH_{AB} for the free expansion of an ideal gas.

b) Find ΔU_{AB} and ΔH_{AB} for the free expansion of a hard sphere gas, which is the van der Waals gas with $a = 0$, $b > 0$.

Express your results in terms of T_A, V_A, V_B, and N. For both the ideal gas and the hard sphere gas the equation of state for temperature is $T = U/(c_V M)$; assume c_V is constant.

Solution First note that this free expansion is an irreversible process. It's also an example of a process that is *not* quasi-static. Nevertheless, internal energy and enthalpy only depend on the state of the system at equilibrium, not on the process by which it reached that state.

(a) The system is isolated so $U_A = U_B$ thus $\Delta U_{AB} = 0$. For a pure ideal gas $U = c_V MT$ so $T_A = T_B$. Since the temperature does not change during a free expansion we have from the ideal gas law that $p_A V_A = p_B V_B$ so

$$\Delta H_{AB} = (U_B + p_B V_B) - (U_A + p_A V_A) = 0$$

(b) Again $\Delta U_{AB} = 0$ because the system is isolated. We also have $U = c_V MT$ so $T_A = T_B$. However,

$$pV = \left(\frac{N\mathrm{R}T}{V - Nb} \right) V = N\mathrm{R}T\frac{V}{V - Nb}$$

so

$$\Delta H_{AB} = p_B V_B - p_A V_A = N\mathrm{R}T_A \left(\frac{V_B}{V_B - Nb} - \frac{V_A}{V_A - Nb} \right) = N\mathrm{R}T_A \left(\frac{-Nb(V_B - V_A)}{(V_B - Nb)(V_A - Nb)} \right) \leq 0$$
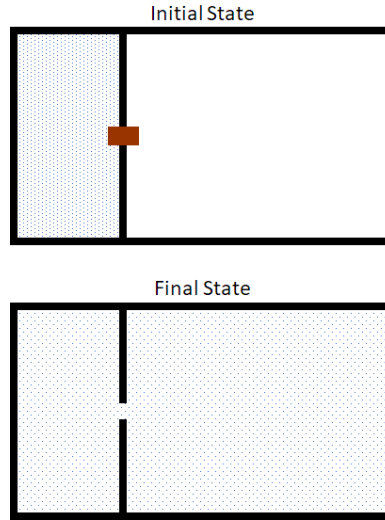

Figure 4: Free expansion of a gas in a heterogeneous isolated system.

Example The molar heat capacity of a diatomic gas is often approximated as $\hat{c}_V = (f/2)R$ with $f = 5$ classical degrees of freedom (three translational plus two rotational). A more accurate approximation, which includes molecular vibration, is

$$\hat{c}_V(T) = \frac{5}{2}R + \frac{\theta_v^2}{T^2} \frac{R\ e^{\theta_v/T}}{(e^{\theta_v/T} - 1)^2}$$

where θ_v is a vibrational temperature.

(a) Show that $\hat{c}_V(T) \approx (5/2)R$ for $T \ll \theta_v$ and $\hat{c}_V(T) \approx (7/2)R$ for $T \gg \theta_v$.

(b) Plot $\hat{c}_V(T)/R$ versus T from 250 K to 1000 K for nitrogen gas ($\theta_v = 3340$ K) and chlorine gas ($\theta_v = 810$ K).

Solution (a) For $T \ll \theta_v$,

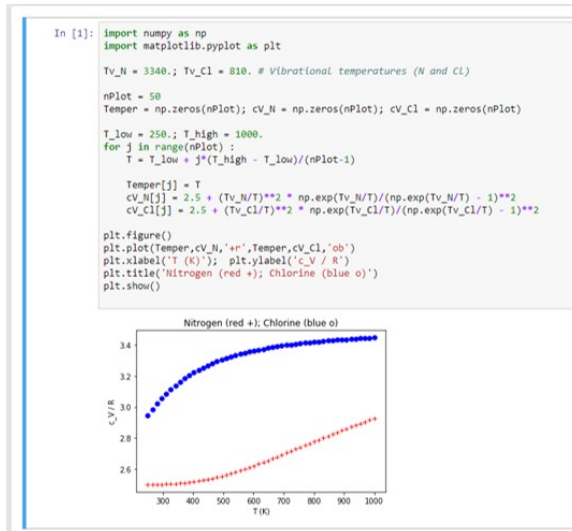$$\hat{c}_V(T) \approx \frac{5}{2}R + \frac{\theta_v^2}{T^2}R\ e^{-\theta_v/T}$$

so the last term becomes exponentially small. For the other limit, using Mathematica or Wolfram Alpha we get the following series expansions about $x = 0$,

$$x^2 \frac{e^x}{(e^x - 1)^2} = 1 - \frac{x^2}{12} + \dots$$

For $|x| = \theta_v/T \ll 1$ this goes to one, which gives the desired result.

(b) Here is a python script that creates the graph:

```
In [1]: import numpy as np
        import matplotlib.pyplot as plt

        Tv_N = 3340.; Tv_Cl = 810. # Vibrational temperatures (N and Cl)

        nPlot = 50
        Temper = np.zeros(nPlot); cV_N = np.zeros(nPlot); cV_Cl = np.zeros(nPlot)

        T_low = 250.; T_high = 1000.
        for j in range(nPlot) :
            T = T_low + j*(T_high - T_low)/(nPlot-1)

            Temper[j] = T
            cV_N[j] = 2.5 + (Tv_N/T)**2 * np.exp(Tv_N/T)/(np.exp(Tv_N/T) - 1)**2
            cV_Cl[j] = 2.5 + (Tv_Cl/T)**2 * np.exp(Tv_Cl/T)/(np.exp(Tv_Cl/T) - 1)**2

        plt.figure()
        plt.plot(Temper,cV_N,'+r',Temper,cV_Cl,'ob')
        plt.xlabel('T (K)');  plt.ylabel('c_V / R')
        plt.title('Nitrogen (red +); Chlorine (blue o)')
        plt.show()
```


From Wikipedia $\hat{c}_p = 29.1$ J/(mol K) for nitrogen and 33.9 J/(mol K) for chlorine so $\hat{c}_V = \hat{c}_p - R = 2.5R$ for nitrogen and 3.1R for chlorine. These values match those in the plot for 300 Kelvin.

Chapter 5: Entropy

Example The following relations are known for a monatomic ideal gas,

$$pV = NRT \qquad U = \frac{3}{2}NRT \qquad S = NR\ln(U^{3/2}VN^{-5/2}) + Ns_0$$

where s_0 is a constant. Find the isothermal and the adiabatic bulk modulus, which are defined as,

$$b_T = -V\left(\frac{\partial p}{\partial V}\right)_{T,N} \qquad \text{and} \qquad b_S = -V\left(\frac{\partial p}{\partial V}\right)_{S,N}$$

Note that the bulk modulus is analogous to the "spring constant" for a material. Hint: Use the cyclic chain rule to evaluate b_S.

Solution The isothermal bulk modulus is easy to get since

$$\left(\frac{\partial p}{\partial V}\right)_{T,N} = \left(\frac{\partial}{\partial V}\right)_{T,N}\left(\frac{NRT}{V}\right) = -\frac{NRT}{V^2} = -\frac{p}{V}$$

so $b_T = p$. To get the adiabatic bulk modulus the first step is to write $S(p,V,N)$, which is easy since $U = \frac{3}{2}NRT = \frac{3}{2}pV$ so

$$S(p,V,N) = NR\ln(p^{3/2}V^{5/2}) + f(N)$$

where $f(N)$ only depends on N. Using the hint we write,

$$\left(\frac{\partial p}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N}\left(\frac{\partial S}{\partial V}\right)_{p,N}$$

The first term is easier to evaluate by flipping the derivatives,

$$\left(\frac{\partial p}{\partial S}\right)_{V,N} = \frac{1}{\left(\frac{\partial S}{\partial p}\right)_{V,N}} = \frac{1}{\frac{3}{2}NR/p}$$

The other term is

$$\left(\frac{\partial S}{\partial V}\right)_{p,N} = \frac{5}{2}NR/V$$

Putting it all together,

$$\left(\frac{\partial p}{\partial V}\right)_{S,N} = -\left(\frac{1}{\frac{3}{2}NR/p}\right)\left(\frac{5}{2}NR/V\right) = -\frac{5}{3}\frac{p}{V}$$

so $b_S = \frac{5}{3}p$.

Example Your lab has received a sample (mass M) of Sanjosenium, an exotic, inert solid. From databases you find that its coefficient of thermal expansion and specific heat capacity at constant pressure are functions of temperature. Specifically,

$$\alpha(T) = \alpha_0 + \alpha_1(T - T_0) \qquad \text{and} \qquad c_p(T) = c_0 + c_1(T - T_0)$$

where α_0, α_1, c_0, and c_1 are known constants; T_0 is a reference temperature. You also know that the mass density of Sanjosenium is ρ_0 at $T = T_0$. As part of your analysis the sample is slowly heated from $T_A = T_0$ to $T_B = T_0 + \Delta T$ while at constant pressure p_0 (i.e., by a quasi-static, isobaric process).

(a) Find Q_{AB}, the heat added to the sample during this process.

(b) Find W_{AB}, the work done on the sample during this process. Hint: use the linear approximation for the volume of a solid, $V(T, p, M) = V_0[1 + \alpha(T)(T - T_0)]$ at constant pressure.

(c) Find ΔU_{AB} and ΔH_{AB}, the changes in internal energy and enthalpy.

(d) Find ΔS_{AB}, the change in entropy.

Solution (a) The heat added is,

$$Q_{AB} = \int_A^B dQ = \int_A^B \frac{dQ}{dT} \, dT = \int_A^B C_p \, dT = \int_A^B Mc_p \, dT$$

$$= M \int_{T_0}^{T_0+\Delta T} c_0 + c_1(T - T_0) \, dT = M \left(c_0 \Delta T + \frac{1}{2} c_1 \Delta T^2 \right)$$

(b) The work done is,

$$W_{AB} = -\int_A^B p dV = -p_0 \int_A^B \frac{dV}{dT} \, dT$$

$$= -p_0 \int_{T_0}^{T_0+\Delta T} V_0 \left(\alpha(T) + \frac{d\alpha}{dT}(T - T_0) \right) \, dT$$

$$= -p_0 V_0 \int_{T_0}^{T_0+\Delta T} \alpha_0 + 2\alpha_1(T - T_0) \, dT$$

$$= -p_0 V_0 (\alpha_0 + \alpha_1 \Delta T) \Delta T$$

Note that $V_0 = M/\rho_0$.

(c) Using the results from parts (a) and (b), by First Law $\Delta U_{AB} = Q_{AB} + W_{AB}$. Since the quasi-static process was at constant pressure $\Delta H_{AB} = Q_{AB}$. Note that being state variables ΔU_{AB} and ΔH_{AB} are the same for *all* processes going from state A to state B, even non-equilibrium processes.

(d) The change in entropy is,

$$\Delta S_{AB} = \int_A^B \frac{dQ}{T} = \int_A^B \frac{Mc_p}{T} \, dT = M \int_{T_0}^{T_0+\Delta T} \frac{c_0 + c_1(T - T_0)}{T} \, dT$$

$$= M(c_0 - c_1 T_0) \ln(1 + \Delta T/T_0) + c_1 \Delta T$$

Example (a) The heat capacity of a certain material is measured to be,

$$C_p = a + bT = (20.35 \text{ J/K}) + (0.2 \text{ J/K}^2) \, T$$

Calculate the change in entropy for a reversible, isobaric (constant pressure) process that increased the temperature from 298.15 Kelvin to 304.0 Kelvin.

(b) A system at 70 degrees Celsius is in thermal contact with another system at 25 degrees Celsius. During a time of 0.23 seconds the amount of heat exchanged is 0.5 Joules. The systems have large heat capacities so the exchange of energy during this irreversible process has a negligible effect on their temperatures. Find the total change of entropy and the rate of change of entropy, $d_i S/dt$.

Solution (a) Since $C_p = (dQ/dT)_p$, for this reversible process,

$$dS = d_e S = \frac{dQ}{T} = \frac{C_p dT}{T}$$

Since $C_p = a + bT$,

$$\Delta S = \int_{T_i}^{T_f} dS = \int_{T_i}^{T_f} \frac{a + bT}{T} dT = a \ln(T_f/T_i) + b(T_f - T_i)$$

Inserting the numerical values we get $\Delta S = 1.6$ J/K.

(b) We may consider the two large bodies as a single isolated system so this irreversible process results in a change of entropy,

$$\Delta S = \int_A^B d_i S = \int_A^B dS^{\text{cold}} + \int_A^B dS^{\text{hot}} = \int_A^B \frac{dQ^{\text{cold}}}{T^{\text{cold}}} + \int_A^B \frac{dQ^{\text{hot}}}{T^{\text{hot}}} = \left(\frac{1}{T^{\text{cold}}} - \frac{1}{T^{\text{hot}}} \right) \int_A^B dQ$$

Here we've used the fact that the amount of energy lost by the hot body equals the amount of energy gained by the cold one so $Q_{AB}^{\text{cold}} = -Q_{AB}^{\text{hot}}$. Since $\int_A^B dQ = Q_{AB} = 0.5$ J, putting in the numerical values gives $\Delta S = 2.2 \times 10^{-4}$ J/K. If this occurs in $\Delta t = 0.23$ seconds then $d_i S/dt = \Delta S/\Delta t = 9.6 \times 10^{-4}$ J/K·s.

Example Given that for a pure ideal gas the entropy is

$$S(T, V, M) = M\left[s_0 + \frac{k_B}{m} \ln(V/M) + c_V \ln(T)\right]$$

show that $S(T_A, V_A, N) = S(T_B, V_B, N)$ when $T_A V_A^{\gamma-1} = T_B V_B^{\gamma-1}$ where $\gamma = c_p/c_V$.

Solution Start by writing

$$S(T, V, M) = M\left[s_0 - \frac{k_B}{m} \ln(M) + \ln\left(T^{c_V} V^{k_B/m}\right)\right]$$

Next, write,

$$TV^{\gamma-1} = TV^{c_p/c_V - 1} = TV^{(c_p - c_V)/c_V} = TV^{k_B/mc_V}$$

since for an ideal gas $c_p - c_V = k_B/m$. Finally, write $T_A V_A^{\gamma-1} = T_B V_B^{\gamma-1}$ as $T_A V_A^{k_B/mc_V} = T_B V_B^{k_B/mc_V}$ and raise it to the c_V power,

$$\left(T_A V_A^{k_B/mc_V}\right)^{c_V} = \left(T_B V_B^{k_B/mc_V}\right)^{c_V}$$

and we have $T_A^{c_V} V_A^{k_B/m} = T_B^{c_V} V_B^{k_B/m}$ so $S_A = S_B$ by inspection.

Example An isolated system is divided into two parts by a removable partition. Initially both parts contain different monatomic ideal gases ($\hat{c}_V = \frac{3}{2}R$). The left side has $N_L = 3.0$ moles of helium in a volume of $V_L = 3.0$ liters at $T_L = 400$ K while the right side has $N_R = 1.0$ moles of argon in a volume of $V_R = 5.0$ liters at $T_R = 800$ K.

(a) Find the final temperature and pressure in the system after the partition is removed and the gas mixture reaches equilibrium.

(b) Find the total change in the entropy from the initial to the final state. Note that since the gases are ideal even after mixing you may calculate their entropies by treat them independently then sum those entropies for the total entropy in the system.

(c) Repeat part (b) for an initial state of $N_L = 2.0$ moles of helium, $N_R = 2.0$ moles of argon, with $V_L = V_R = 4.0$ liters and $T_L = T_R = 500$ K.

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Solution (a) The internal energy is $U = \frac{3}{2}NRT$ and it is constant in this isolated system so,

$$\frac{3}{2}N_{\mathrm{L}}RT_{\mathrm{L}} + \frac{3}{2}N_{\mathrm{R}}RT_{\mathrm{R}} = \frac{3}{2}(N_{\mathrm{L}} + N_{\mathrm{R}})RT_{\Sigma}$$

so the final temperature is,

$$T_{\Sigma} = \frac{N_{\mathrm{L}}T_{\mathrm{L}} + N_{\mathrm{R}}T_{\mathrm{R}}}{N_{\mathrm{L}} + N_{\mathrm{R}}} = 500 \text{ K}$$

Since $V_{\Sigma} = V_{\mathrm{L}} + V_{\mathrm{R}}$ the final pressure is $p_{\Sigma} = (N_{\mathrm{L}} + N_{\mathrm{R}})RT_{\Sigma}/V_{\Sigma} = 2100$ kPa.

(b) The entropy is,

$$S(T, V, N) = N\{s_0 + \hat{c}_V \ln(T) + R \ln(V/N)\}$$

For a monatomic ideal gas $C_V = \frac{3}{2}NR$ so the initial entropy of the system is,

$$
\begin{aligned}
S_i &= S^{\mathrm{He}}(T_{\mathrm{L}}, V_{\mathrm{L}}, N_{\mathrm{L}}) + S^{\mathrm{Ar}}(T_{\mathrm{R}}, V_{\mathrm{R}}, N_{\mathrm{R}}) \\
&= N_{\mathrm{L}}\{s_0^{\mathrm{He}} + \tfrac{3}{2}R \ln(T_{\mathrm{L}}) + R \ln(V_{\mathrm{L}}/N_{\mathrm{L}})\} + N_{\mathrm{R}}\{s_0^{\mathrm{Ar}} + \tfrac{3}{2}R \ln(T_{\mathrm{R}}) + R \ln(V_{\mathrm{R}}/N_{\mathrm{R}})\}
\end{aligned}
$$

Similarly, after mixing the final entropy is,

$$
\begin{aligned}
S_f &= S^{\mathrm{He}}(T_{\Sigma}, V_{\Sigma}, N_{\mathrm{L}}) + S^{\mathrm{Ar}}(T_{\Sigma}, V_{\Sigma}, N_{\mathrm{R}}) \\
&= N_{\mathrm{L}}\{s_0^{\mathrm{He}} + \tfrac{3}{2}R \ln(T_{\Sigma}) + R \ln(V_{\Sigma}/N_{\mathrm{L}})\} + N_{\mathrm{R}}\{s_0^{\mathrm{Ar}} + \tfrac{3}{2}R \ln(T_{\Sigma}) + R \ln(V_{\Sigma}/N_{\mathrm{R}})\}
\end{aligned}
$$

The change in entropy is,

$$S_f - S_i = \tfrac{3}{2}R\{N_{\mathrm{L}} \ln(T_{\Sigma}/T_{\mathrm{L}}) + N_{\mathrm{R}} \ln(T_{\Sigma}/T_{\mathrm{R}})\} + R\{N_{\mathrm{L}} \ln(V_{\Sigma}/V_{\mathrm{L}}) + N_{\mathrm{R}} \ln(V_{\Sigma}/V_{\mathrm{R}})\} = 30.9 \text{ J/K}$$

(c) In this case the temperature is unchanged by the mixing (i.e., $T_{\Sigma} = T_{\mathrm{L}} = T_{\mathrm{R}}$) and $V_{\mathrm{L}} = V_{\mathrm{R}} = \frac{1}{2}V_{\Sigma}$ so

$$S_f - S_i = R\{N_{\mathrm{L}} \ln(2) + N_{\mathrm{R}} \ln(2)\} = RN_{\Sigma} \ln(2) = 23.0 \text{ J/K}$$

The change of entropy in this case (equal temperature and density) is called the "entropy of mixing".

Example Using the condition $S(T, \lambda V, \lambda N) = \lambda S(T, V, N)$ show that

$$S(T, V, N) = S_0(T_0, V_0, N) + NR \ln(V/V_0) + c_V M \ln(T/T_0)$$

may be written as

$$S(T, V, N) = N[s_0 + R \ln(V/N) + c_V m N_{\mathrm{A}} \ln T]$$

Solution We start with the expression,

$$S(T, V, N) = S(T_0, V_0, N) + c_V m N N_{\mathrm{A}} \ln(T/T_0) + NR \ln(V/V_0)$$

since $M = m\mathcal{N} = mNN_{\mathrm{A}}$. Apply the condition $S(T, \lambda V, \lambda N) = \lambda S(T, V, N)$,

$$S(T_0, V_0, \lambda N) + C_{Vm}\lambda N \ln(T/T_0) + \lambda NR \ln(\lambda V/V_0) = \lambda\{S(T_0, V_0, N) + \lambda c_V m N N_{\mathrm{A}} \ln(T/T_0) + \lambda NR \ln(V/V_0)\}$$

Differentiate both sides by $d/d\lambda$,

$$\frac{dS(T_0, V_0, \lambda N)}{d\lambda} + C_{Vm}N \ln(T/T_0) + NR \ln(\lambda V/V_0) + NR = S(T_0, V_0, N) + \lambda c_V m N N_{\mathrm{A}} \ln(T/T_0) + \lambda NR \ln(V/V_0)$$

The first term simplifies to,

$$\frac{dS(T_0, V_0, \lambda N)}{d\lambda} = \frac{dS(T_0, V_0, \lambda N)}{d(\lambda N)} \frac{d(\lambda N)}{d\lambda} = \frac{dS(T_0, V_0, \lambda N)}{d(\lambda N)} N$$

Inserting this into the previous expression and setting $\lambda = 1$ gives,

$$\frac{dS(T_0, V_0, N)}{dN} N + C_{Vm} N \ln(T/T_0) + N\mathrm{R}\ln(V/V_0) + N\mathrm{R} = S(T_0, V_0, N) + c_V m N \mathrm{N_A} \ln(T/T_0) + N\mathrm{R}\ln(V/V_0)$$

Writing $S(T_0, V_0, N) = f(N)$ this is an inhomogeneous ordinary differential equation,

$$N\frac{df}{dN} + N\mathrm{R} = f$$

which has solution,

$$f(N) = \mathcal{C}N - N\mathrm{R}\ln(N)$$

where $\mathcal{C}$ is a constant. Combining the above,

$$\begin{aligned} S(T, V, N) &= \mathcal{C}N - N\mathrm{R}\ln(N) + C_{Vm}N\ln(T/T_0) + N\mathrm{R}\ln(V/V_0) \\ &= N\{s_0 + c_V m \mathrm{N_A}\ln(T) + \mathrm{R}\ln(V/N)\} \end{aligned}$$

with $s_0 = \mathcal{C} - c_V m \mathrm{N_A} c_V m \mathrm{N_A} \ln(T_0) - \mathrm{R}\ln(V_0)$.

Chapter 6: Reversible and Irreversible Processes

Example Consider a heterogeneous isolated system consisting of an inert rock and a thermal reservoir at temperature T^{res}. The initial temperature of the rock is $T = T_0$ and being in contact with the reservoir this temperature changes with time, specifically,

$$T(t) = T_0 + (1 - e^{-t/\tau})\Delta T$$

where $\Delta T = T^{\text{res}} - T_0$ and τ is a constant. The volume of the rock and reservoir remain constant so there is heat but no work. The heat capacity of the rock, C_V, is constant.

(a) Find dS/dt for the rock. From your expression verify that if the rock is initially colder than the reservoir ($T_0 < T^{\text{res}}$) then $dS/dt > 0$ with $dS/dt \to 0$ as $t \to \infty$.

(b) Find dS^{res}/dt for the reservoir. From your expression verify that if $T_0 < T^{\text{res}}$ then $dS^{\text{res}}/dt < 0$ with $dS^{\text{res}}/dt \to 0$ as $t \to \infty$.

(c) Find dS^{Σ}/dt where $S^{\Sigma} = S + S^{\text{res}}$ is the entropy of the entire system. From your expression verify that if $T_0 < T^{\text{res}}$ then $dS^{\Sigma}/dt > 0$ with $dS^{\Sigma}/dt \to 0$ as $t \to \infty$.

(d) Verify that if the rock is initially hotter than the reservoir ($T_0 > T^{\text{res}}$) then $dS/dt < 0$, $dS^{\text{res}}/dt > 0$, and $dS^{\Sigma}/dt > 0$. That is, the total entropy of the isolated system increases whether the rock is initially hotter or colder than the reservoir.

Solution (a) For the rock $dS = d_e S = dQ/T$ and $dQ = dU$ since no work is done. Since $U(t) = C_V T(t)$ then

$$\frac{dS}{dt} = \frac{1}{T}\frac{dQ}{dt} = \frac{1}{T}\frac{dU}{dt} = \frac{C_V}{T}\frac{dT}{dt}$$

or

$$\frac{dS}{dt} = \frac{C_V}{T(t)}\frac{\Delta T}{\tau}e^{-t/\tau}$$

If $T_0 < T^{\text{res}}$ then $\Delta T > 0$ so $dS/dt > 0$ by inspection. As $t \to \infty$ we have $T(t) \to T^{\text{res}}$ and $e^{-t/\tau} \to 0$ so $dS/dt \to 0$.

(b) For the reservoir $dS^{\text{res}} = d_e S^{\text{res}} = dQ^{\text{res}}/T^{\text{res}}$ but by conservation of energy $dQ^{\text{res}} = -dQ$ so

$$\frac{dS^{\text{res}}}{dt} = \frac{1}{T^{\text{res}}}\frac{-dQ}{dt} = -\frac{C_V}{T^{\text{res}}}\frac{\Delta T}{\tau}e^{-t/\tau}$$

If $T_0 < T^{\text{res}}$ then $\Delta T > 0$ so $dS^{\text{res}}/dt < 0$ by inspection. Again, due to the decaying exponential $dS^{\text{res}}/dt \to 0$ as $t \to \infty$.

(c) For the total system,

$$\frac{dS^{\Sigma}}{dt} = \frac{dS}{dt} + \frac{dS^{\text{res}}}{dt} = \frac{C_V \Delta T}{\tau}\left(\frac{1}{T(t)} - \frac{1}{T^{\text{res}}}\right)e^{-t/\tau}$$

If $T_0 < T^{\text{res}}$ then $\Delta T > 0$ and $(1/T(t) - 1/T^{\text{res}}) > 0$ so $dS^{\Sigma}/dt > 0$. Again, due to the decaying exponential $dS^{\Sigma}/dt \to 0$ as $t \to \infty$.

(d) If $T_0 > T^{\text{res}}$ then $\Delta T < 0$ and $(1/T(t) - 1/T^{\text{res}}) < 0$; this flips the sign for the results in parts (a) and (b) but not in part (c).

Example A pure, inert, homogeneous system consists of N moles of an ideal gas initially at pressure p_A and temperature T_A. The system undergoes an isothermal, quasi-static expansion until it reaches pressure p_B ($p_A > p_B$). During this expansion it is in contact with a hot reservoir $T^{\text{hot}} = T_A = T_B$.

Next, the hot reservoir is replaced with a cold reservoir at temperature T^{cold}. The volume is held fixed until the pressure drops quasi-statically to p_C at which point the system temperature is $T_C = T^{\text{cold}}$. Finally, the system undergoes an adiabatic compression that returns it to its initial state, p_A and T_A.

(a) Draw a sketch on the $p - V$ diagram showing the total process of $A \rightarrow B \rightarrow C$.

(b) Find ΔS_{AB}, the entropy change for the system in terms of p_A and p_B.

(c) Find $\Delta S_{AB}^{\text{hot}}$, the entropy change for hot reservoir in terms of p_A and p_B.

(d) Find ΔS_{BC}, the entropy change for the system in terms of p_B, p_C, and $\hat{c}_V$.

(e) Find $\Delta S_{BC}^{\text{cold}}$, the entropy change for cold reservoir in terms of p_B, p_C, and $\hat{c}_V$.

(f) The total change in entropy for the system and reservoirs is

$$\Delta S_{\circlearrowright}^{\Sigma} = \Delta S_{\circlearrowright} + \Delta S_{\circlearrowright}^{\text{hot}} + \Delta S_{\circlearrowright}^{\text{cold}}$$

Show that $\Delta S_{\circlearrowright}^{\Sigma} > 0$, which means that the total process is irreversible. Hint: $\ln x \leq x - 1$ for $x > 1$.

Solution (a) The sketch is the same as Figure 6.5 (pg. 50 in the book) but with the cycle going clockwise rather than counter-clockwise. The labels for states B and C are also switched. Note that in Example 6.3 from the book only a single reservoir is used whereas in the present case there are two reservoirs.

(b) For the isothermal expansion from A to B,

$$\Delta S_{AB} = \int_A^B \frac{dQ}{T} = \frac{1}{T^{\text{hot}}} \int_A^B dQ$$

$$= \frac{Q_{AB}}{T^{\text{hot}}} = \frac{W_{AB}}{T^{\text{hot}}} = \frac{NRT^{\text{hot}} \ln(V_B/V_A)}{T^{\text{hot}}} = NR \ln(p_A/p_B)$$

where we used the result from Example 3.3 and the ideal gas law.

(c) Similarly,

$$\Delta S_{AB}^{\text{hot}} = \int_A^B \frac{dQ^{\text{hot}}}{T} = \frac{1}{T^{\text{hot}}} \int_A^B dQ^{\text{hot}}$$

$$= \frac{Q_{AB}^{\text{hot}}}{T^{\text{hot}}} = -\frac{Q_{AB}}{T^{\text{hot}}} = -NR \ln(p_A/p_B)$$

since $Q_{AB}^{\text{hot}} = -Q_{AB}$, that is, the energy that enters the system equals the energy that leaves the reservoir. Note that the path $A \rightarrow B$ is reversible since $\Delta S_{AB} + \Delta S_{AB}^{\text{hot}} = 0$, as expected for isothermal paths.

(d) For the isochoric cooling process the temperature is *not* constant but since the volume is constant,

$$\Delta S_{BC} = \int_B^C \frac{dQ}{T} = \int_B^C \frac{dQ/dT}{T} dT = \int_B^C \frac{C_V}{T} dT$$

$$= N\hat{c}_V \int_B^C \frac{dT}{T} = N\hat{c}_V \ln(T_C/T_B) = N\hat{c}_V \ln(p_C/p_B)$$

(e) As in part (c),

$$\Delta S_{BC}^{\text{cold}} = \frac{Q_{BC}^{\text{cold}}}{T^{\text{cold}}} = -\frac{Q_{BC}}{T^{\text{cold}}} = -\frac{\Delta U_{BC}}{T^{\text{cold}}}$$

Because volume is constant no work is done so the heat added to the cold reservoir equals the change in internal energy by the First Law. For an ideal gas $U(T, V, N) = N\hat{c}_V T$ so,

$$\Delta S_{BC}^{\text{cold}} = -\frac{N\hat{c}_V(T_C - T_B)}{T^{\text{cold}}} = -N\hat{c}_V(1 - T_B/T_C) = N\hat{c}_V(p_B/p_C - 1)$$

since $T^{\text{cold}} = T_C$ and, again, using the ideal gas law.

(f) We need to evaluate,

$$\Delta S_{\circlearrowleft}^{\Sigma} = \Delta S_{\mathrm{AB}} + \Delta S_{\mathrm{AB}}^{\mathrm{hot}} + \Delta S_{\mathrm{BC}} + \Delta S_{\mathrm{BC}}^{\mathrm{cold}} + \Delta S_{\mathrm{CA}}$$
$$= \Delta S_{\mathrm{BC}} + \Delta S_{\mathrm{BC}}^{\mathrm{cold}}$$

since from from parts (b) and (c) we know that $\Delta S_{\mathrm{AB}} + \Delta S_{\mathrm{AB}}^{\mathrm{hot}} = 0$ and $\Delta S_{\mathrm{CA}} = 0$ since that path is adiabatic. From parts (d) and (e) and using the hint,

$$\Delta S_{\circlearrowleft}^{\Sigma} = N\hat{c}_V \ln(p_{\mathrm{C}}/p_{\mathrm{B}}) + N\hat{c}_V (p_{\mathrm{B}}/p_{\mathrm{C}} - 1)$$
$$= N\hat{c}_V [-\ln(p_{\mathrm{B}}/p_{\mathrm{C}}) + p_{\mathrm{B}}/p_{\mathrm{C}} - 1] > 0$$

since $p_{\mathrm{B}} > p_{\mathrm{C}}$.

Chapter 7: Second Law of Thermodynamics

Example A heterogeneous isolated system consists of two pure subsystems, L and R, connected by a conductive, mobile wall (i.e., can exchange energy and volume); see Figure 5. The entropy for subsystem L is $S_L(U_L, V_L, M_L) = (k_B M_L/m) \ln(\mathcal{C}_L U_L^a V_L^b)$; similarly, for subsystem R, $S_R(U_R, V_R, M_R) = (k_B M_R/m) \ln(\mathcal{C}_R U_R^c V_R^d)$. These subsystems are *not* ideal gases and the coefficients a, b, c, d, $\mathcal{C}_L$, and $\mathcal{C}_R$ are constants.
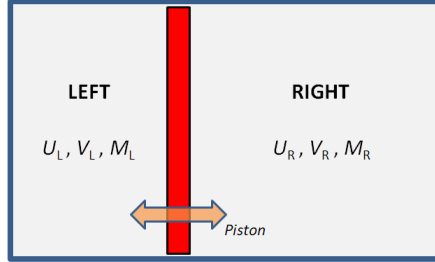

Figure 5: Heterogeneous isolated system with two pure subsystems sharing a conductive, mobile wall.

(a) Obtain expressions for the equations of state of temperature, $T_L(U_L, V_L, M_L)$, and pressure, $p_L(U_L, V_L, M_L)$, for subsystem L.

(b) The subsystems are coupled to each other but isolated from the rest of the world so the total energy, $U_\Sigma = U_L + U_R$, and total volume $V_\Sigma = V_L + V_R$ are constant. Show that at thermodynamic equilibrium the two subsystems are at a common temperature and pressure.

(c) Find the energy and volume, U_L and V_L, of subsystem L at thermodynamic equilibrium in terms of U_Σ, V_Σ, M_L, M_R, and the constants a, b, c, d.

Solution a) The temperature for subsystem L can be obtained from

$$\frac{1}{T_L} = \left(\frac{\partial S_L}{\partial U_L}\right)_{V_L, N_A} = \left(\frac{\partial}{\partial U_L}\right)_{V_L, M_L} (k_B M_L/m) \ln(\mathcal{C}_L U_L^a V_L^b) = \frac{a k_B M_L}{m U_L}$$

so $T_L = m U_L/a k_B M_L$. Similarly for the pressure,

$$\frac{p_L}{T_L} = \left(\frac{\partial S_L}{\partial V_L}\right)_{U_L, M_L} = \left(\frac{\partial}{\partial V_L}\right)_{U_L, M_L} (k_B M_L/m) \ln(\mathcal{C}_L U_L^a V_L^b) = \frac{b k_B M_L}{m V_L}$$

so

$$p_L = \frac{b k_B M_L T_L}{m V_L} = \frac{b U_L}{a V_L}$$

The results are the same for subsystem R, replacing a and b with c and d, respectively.

b) In the entropy representation the Gibbs equation for each subsystem is,

$$dS_L = \frac{1}{T_L} dU_L + \frac{p_L}{T_L} dV_L \qquad \text{and} \qquad dS_R = \frac{1}{T_R} dU_R + \frac{p_R}{T_R} dV_R$$

since $dM_L = 0$ and $dM_R = 0$. The total entropy, $S_\Sigma = S_L + S_R$ so

$$dS_\Sigma = dS_L + dS_R = \left(\frac{1}{T_R} - \frac{1}{T_L}\right) dU_R + \left(\frac{p_R}{T_R} - \frac{p_L}{T_L}\right) dV_R$$

since $dU_L = -dU_R$ and $dV_L = -dV_R$ by conservation of energy and volume. We identify the thermodynamic forces for energy and volume to be,

$$F_U = \frac{1}{T_R} - \frac{1}{T_L} \qquad\qquad F_V = \frac{p_R}{T_R} - \frac{p_L}{T_L}$$

These are zero at thermodynamic equilibrium so that condition is met when the two sides have equal temperatures and pressures.

c) Since $T_L = T_R$ and $U_R = U_\Sigma - U_L$,

$$\frac{a k_B M_L}{m U_L} = \frac{c k_B M_R}{m(U_\Sigma - U_L)}$$

so

$$U_L = \frac{a M_L}{a M_L + c M_R} U_\Sigma$$

Similarly, since $p_L = p_R$ and $V_R = V_\Sigma - V_L$,

$$\frac{b k_B M_L T_L}{m V_L} = \frac{d k_B M_R T_R}{m(V_\Sigma - V_L)}$$

so

$$V_L = \frac{b M_L}{b M_L + d M_R} V_\Sigma$$

Notice that if the two systems are identical ($a = c$, $b = d$, and $M_L = M_R$) then they split the energy and volume by 50-50.

Example A theoretical calculation predicts that the energy for certain pure substance is,

$$U(S, V, M) = \mathcal{A}(SVM)^{1/3}$$

where $\mathcal{A}$ is a physical constant.

(a) Find the temperature, $T(U, V, M)$, in terms of internal energy, volume, and mass. What is unusual about this result?

(b) Find the pressure, $p(T, V, M)$, in terms of temperature, volume, and mass. What is unusual about this result?

(c) A revised theoretical calculation gives $U = \mathcal{A}(VM/S)^{1/3}$ but you immediately know this cannot be correct. Why?

Solution (a) First, the temperature may be found using,

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,\mathbf{M}} = \frac{1}{3}\mathcal{A}S^{-2/3}V^{1/3}M^{1/3}$$

However this is $T(S, V, M)$ and we want $T(U, V, M)$. To make the change of variable we use

$$S = \frac{U^3}{\mathcal{A}^3 V M}$$

so

$$T(U, V, M) = \frac{1}{3}\mathcal{A}\left(\frac{U^3}{\mathcal{A}^3 V M}\right)^{-2/3} V^{1/3} M^{1/3} = \frac{1}{3}\mathcal{A}^3\frac{V M}{U^2}$$

Strangely, this predicts that as the internal energy increases (with fixed V and M) the temperature *decreases*.

(b) For the pressure,
$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,M} = \frac{1}{3}\mathcal{A}\frac{(SVM)^{1/3}}{V} = -\frac{U}{3V}$$

From the result in part (a),
$$U = \sqrt{\frac{\mathcal{A}^3 VM}{3T}}$$

so
$$p(T, V, M) = -\sqrt{\frac{\mathcal{A}^3 M}{27VT}}$$

Strangely, this pressure is negative.

(c) The internal energy is an extensive variable so it must be that $U(\lambda S, \lambda V, \lambda M) = \lambda U(S, V, M)$ for any constant λ. The original expression for U is extensive but the revised expression is not so it cannot be correct. Back to the drawing board.

Example (a) Use the Gibbs equation to show that,

$$\left(\frac{\partial}{\partial V}\frac{1}{T}\right)_{U,\mathbf{M}} = \left(\frac{\partial}{\partial U}\frac{p}{T}\right)_{V,\mathbf{M}}$$

(b) For a gas of photons (i.e., blackbody radiation) the equations of state for temperature and pressure are,

$$T = \left(\frac{c_0}{4\sigma_{\text{SB}}}\frac{U}{V}\right)^{1/4} \qquad \text{and} \qquad p = \frac{U}{aV}$$

where c_0 is the speed of light and σ_{SB} is the Stefan-Boltzmann constant. Find the numerical value of the constant a.

Solution (a) From the Gibbs equation in the entropy representation we know that,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,\mathbf{M}} \qquad \text{and} \qquad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,\mathbf{M}}$$

Since $dS(U, V, \mathbf{M})$ is an exact differential we also know that,

$$\frac{\partial^2 S}{\partial U \partial V} = \left(\frac{\partial}{\partial V}\right)_{U,\mathbf{M}}\left(\frac{\partial S}{\partial U}\right)_{V,\mathbf{M}} = \left(\frac{\partial}{\partial U}\right)_{V,\mathbf{M}}\left(\frac{\partial S}{\partial V}\right)_{U,\mathbf{M}}$$

Combining these expressions gives the desired result.

(b) First we write $T = \mathcal{C}U^{1/4}V^{-1/4}$ where $\mathcal{C} = (c_0/4\sigma_{\text{SB}})^{1/4}$ and evaluate,

$$\left(\frac{\partial}{\partial V}\right)_{U,\mathbf{M}}\frac{1}{T} = \left(\frac{\partial}{\partial V}\right)_{U,\mathbf{M}}\mathcal{C}^{-1}U^{-1/4}V^{1/4} = \frac{1}{4}\mathcal{C}^{-1}U^{-1/4}V^{-3/4}$$

Similarly, $p/T = a^{-1}\mathcal{C}^{-1}U^{3/4}V^{-3/4}$ so

$$\left(\frac{\partial}{\partial U}\right)_{V,\mathbf{M}}\frac{p}{T} = \left(\frac{\partial}{\partial U}\right)_{V,\mathbf{M}}a^{-1}\mathcal{C}^{-1}U^{3/4}V^{-3/4} = \frac{3}{4}a^{-1}\mathcal{C}^{-1}U^{-1/4}V^{-3/4}$$

Equating these expressions gives $a = 3$.

Example A theoretical model for a non-ideal pure gas gives,

$$S(U, V, N) = N s_0 + NR \ln\left(\frac{V - bN}{V_0 - bN}\right) + \frac{3}{2}NR \ln(\ \sinh[c\ (U/N + aN/V)]\ )$$

The parameters a, b, c, s_0, and V_0 are constants in the model.
   (a) Find the pressure $p(T, V, N)$.
   (b) Show that the heat capacity at constant volume is,

$$C_V = \frac{\mathcal{C}N}{1 - f(T)}$$

and find explicit expressions for the constant $\mathcal{C}$ and the function $f(T)$. Notice that for this model C_V is a function of temperature (i.e., it is *not* a constant).

   Solution (a) Using

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,M} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$$

then

$$\frac{1}{T} = \frac{3}{2}Rc\frac{\cosh(cU/N + caN/V)}{\sinh(cU/N + caN/V)}$$

so

$$T = \frac{2}{3Rc}\tanh(cU/N + caN/V)$$

   Similarly, using

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}$$

then

$$\begin{aligned}
\frac{p}{T} &= \frac{RN}{V - bN} + \frac{3}{2}R\left(\frac{-caN^2}{V^2}\right)\frac{\cosh(cU/N + caN/V)}{\sinh(cU/N + caN/V)} \\
&= \frac{RN}{V - bN} - \frac{aN^2}{TV^2}
\end{aligned}$$

so

$$\left(p - \frac{aN^2}{V^2}\right)(V - bN) = NRT$$

which is the van der Waals equation of state. Note that the expression given in this exercise for entropy is *not* the only one that give this equation of state for the pressure; you could formulate a different $S(U, V, N)$ that gives the same $p(T, V, N)$.
   (b) We want to find $C_V = (\partial U/\partial T)_{V,N}$. The easiest route is probably to use the equation for temperature in a rather unconventional way,

$$\left(\frac{\partial}{\partial T}\right)_{V,N}T = \left(\frac{\partial}{\partial T}\right)_{V,N}\frac{2}{3Rc}\tanh(cU/N + caN/V)$$

or

$$1 = \frac{2}{3cR}(c/N)\operatorname{sech}^2(cU/N + caN/V)\left(\frac{\partial U}{\partial T}\right)_{V,N}$$

Using the identity,

$$\operatorname{sech}^2(x) = 1 - \tanh^2(x)$$

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then

$$1 = \frac{2}{3\mathrm{R}N}\left[1 - \tanh^2(cU/N + caN/V)\right]\left(\frac{\partial U}{\partial T}\right)_{V,N}$$

$$= \frac{2}{3\mathrm{R}N}\left[1 - (3\mathrm{R}cT/2)^2\right]\left(\frac{\partial U}{\partial T}\right)_{V,N}$$

Finally,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{\frac{3}{2}N\mathrm{R}}{1 - (3\mathrm{R}cT/2)^2}$$

so $\mathcal{C} = 3\mathrm{R}/2$ and $f(T) = (3\mathrm{R}cT/2)^2$.

Example Consider an isolated system divided into two subsystems by a stationary, conducting wall. The two parts are initially at temperatures $T_\mathrm{L} = 500$ K and $T_\mathrm{R} = 300$ K. For each subsystem the internal energy is $U(T) = CT$ where their heat capacities are $C_\mathrm{L} = 200$ J/K and $C_\mathrm{R} = 50$ J/K. The rate of heat flow from subsystem L to R is given by Newton's Law of Cooling,

$$\mathcal{J}_U = \frac{dU_\rightarrow}{dt} = \alpha V(T_\mathrm{L} - T_\mathrm{R})$$

with a coefficient of heat flow equal to $\alpha = 20$ J/Ksm^3).

(a) Find expressions for $T_\mathrm{L}(t)$ and $T_\mathrm{R}(t)$. (Hint: You'll have to solve a simple ordinary differential equation).

(b) Graph your results for $T_\mathrm{L}(t)$ and $T_\mathrm{R}(t)$ from part (a) versus time from $t = 0$ to $t = 10$ s.

(c) The rate of entropy production is,

$$\frac{d_\mathrm{i}S}{dt} = \left(\frac{1}{T_\mathrm{R}} - \frac{1}{T_\mathrm{L}}\right)\left(\frac{dU_\rightarrow}{dt}\right)$$

Graph $d_\mathrm{i}S/dt$ as a function of time from $t = 0$ to $t = 10$ s.

In parts (b) and (c) produce accurate graphs, preferably computer generated, not just rough qualitative sketches.

Solution (a) Since $U_\mathrm{L} = C_\mathrm{L}T_\mathrm{L}$ and $dU_\mathrm{L}/dt = -dU_\rightarrow/dt$ we have an ordinary differential equation for $T_\mathrm{L}(t)$,

$$C_\mathrm{L}\frac{dT_\mathrm{L}}{dt} = -\alpha V(T_\mathrm{L} - T_\mathrm{R}) = -\alpha V\left(1 + \frac{C_\mathrm{L}}{C_\mathrm{R}}\right)T_\mathrm{L} + \alpha V U_\Sigma/C_\mathrm{R}$$

where $U_\Sigma = C_\mathrm{L}T_\mathrm{L}(t = 0) + C_\mathrm{R}T_\mathrm{R}(t = 0)$ is the total energy in the system. This may be written as an ODE in the form,

$$\frac{df}{dt} = -Af(t) + B$$

which has a solution,

$$f(t) = \frac{B}{A} + \left(f(t = 0) - \frac{B}{A}\right)e^{-At}$$

so

$$T_\mathrm{L}(t) = \frac{U_\Sigma}{C_\mathrm{L}(C_\mathrm{L} + C_\mathrm{R})} + \left[T_\mathrm{L}(t = 0) - \frac{U_\Sigma}{C_\mathrm{L}(C_\mathrm{L} + C_\mathrm{R})}\right]\exp\left(-\alpha V\left[\frac{1}{C_\mathrm{L}} + \frac{1}{C_\mathrm{R}}\right]t\right)$$

Having found $T_\mathrm{L}(t)$ we have

$$T_\mathrm{R}(t) = \frac{U_\Sigma - C_\mathrm{L}T_\mathrm{L}(t)}{C_\mathrm{R}}$$

(b,c) The functions T_L, T_R, and $d_\mathrm{i}S/dt$ may be evaluated and plotted using the Mathematica script below; the graphs are shown in Figures 6 and 7.

```
alpha = 20;
temp1i = 500;   temp2i = 300;
cv1 = 200;   cv2 = 50;
uTotal = cv1 temp1i + cv2 temp2i;
aa = alpha/cv1 (1 + cv1/cv2);
bb = alpha uTotal/(cv1 cv2);
cc = temp1i - bb/aa;
temp1[t_]  := bb/aa + cc Exp[-aa t];
temp2[t_]:= (uTotal-cv1 temp1[t])/cv2;
entropyRate[t_] := (1/temp2[t] - 1/temp1[t]) alpha (temp1[t]-temp2[t]);
Plot[{temp1[t],temp2[t]},{t,0,10},PlotRange->Full]
Plot[entropyRate[t],{t,0,10},PlotRange->Full]
```
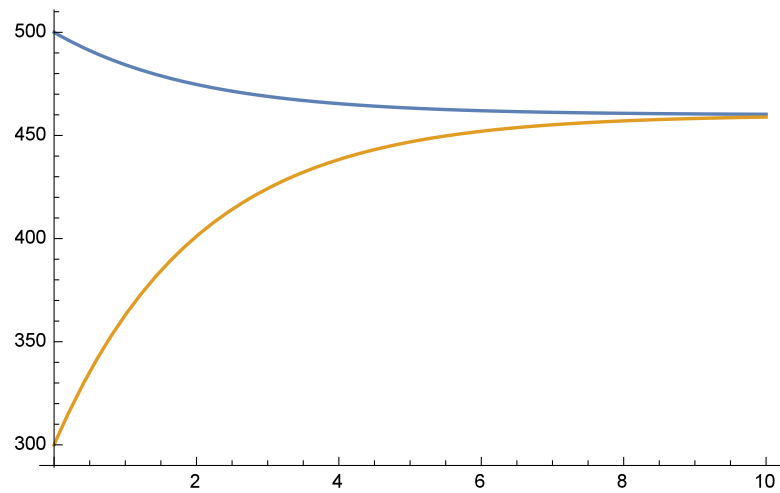

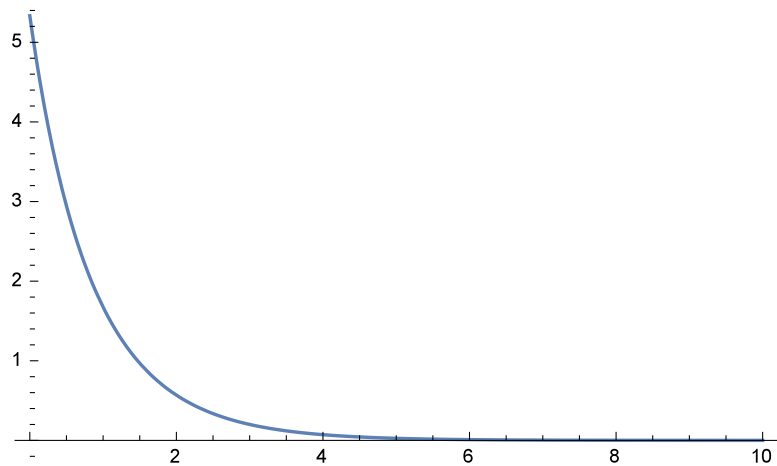Figure 6: Temperature relaxation in time for a heterogenous, isolated system.

Figure 7: Entropy production in time for a heterogenous, isolated system.

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Chapter 8: Thermodynamic Cycles

Example Numerically compute and graph the $p - V$ diagram for a Carnot cycle engine consisting of one mole of an ideal gas with $\gamma = 5/3$. Take the high and low temperatures to be $T_{\text{hot}} = 400$ K and $T_{\text{cold}} = 300$ K; take the high and low pressures on the upper (hot) isothermal branch to be $p_A = 2.0 \times 10^5$ Pa and $p_B = 1.0 \times 10^5$ Pa.

Solution We'll label the four corners of the Carnot cycle A, B, C, and D. We're given $p_A = 2.0 \times 10^5$ Pa and $p_B = 1.0 \times 10^5$ Pa; the temperatures are $T_A = T_B = 400$ K and $T_C = T_D = 300$ K. To create the graphic we need $p(V)$ for each branch as well as the starting and ending values of V on each branch.

The upper isothermal branch gives us $V_A = NRT_A/p_A$ and $V_B = NRT_B/p_B$. Since $TV^{\gamma-1}$ is constant on the adiabatic branches $V_C = (T_B V_B^{\gamma-1}/T_C)^{1/(\gamma-1)}$ and $V_D = (T_A V_A^{\gamma-1}/T_C)^{1/(\gamma-1)}$. From these we can find $p_C = NRT_C/V_C$ and $p_D = NRT_D/V_D$.

For the two isothermal branches pV is constant while on the two adiabatic branches pV^γ is constant so,

$$p_{AB}(V) = \frac{p_A V_A}{V} \qquad p_{BC}(V) = \frac{p_B V_B^\gamma}{V^\gamma} \qquad p_{CD}(V) = \frac{p_C V_C}{V} \qquad p_{DA}(V) = \frac{p_D V_D^\gamma}{V^\gamma}$$

The Mathematica script below produces the graphic shown in Figure 8

```
ClearAll;
R = 8.314; n = 1; gamma = 5/3;
pA = 2 10^5;pB = 1 10^5;
TA = 400; TB = TA; TC = 300; TD = TC;
VA = n R TA/pA;
VB = n R TA/pB;
VC = (VB ^(gamma-1)TB/TC)^(1/(gamma-1));
VD = (VA ^(gamma-1)TA/TD)^(1/(gamma-1));
pC = n R TC/VC;
pD = n R TD/VD;
pAB[V_] := pA (VA/V);
pBC[V_] := pB (VB/V)^gamma;
pCD[V_] := pC (VC/V);
pDA[V_] := pD (VD/V)^gamma;
br1 = Plot[pAB[V],{V,VA,VB},PlotStyle->Red];
br2 = Plot[pBC[V],{V,VB,VC},PlotStyle->Green];
br3 = Plot[pCD[V],{V,VD,VC},PlotStyle->Blue];
br4 = Plot[pDA[V],{V,VA,VD},PlotStyle->Green];
Show[br1,br2,br3,br4,PlotRange-> {{0,VC},{0,pA}},
PlotTheme->"Scientific",AxesOrigin->{0,0}]
```

Example Consider a Carnot heat engine composed of N moles of an ideal gas operating between the temperatures T_{hot} and T_{cold}. a) Find Q_{hot}, the heat added on the isothermal branch from point A to point B (see Figure 8.2 on pg. 67). b) Find $\mathcal{W}_\circlearrowleft$, the work done by the engine in one cycle. c) Show that the efficiency is $\eta = 1 - T_{\text{cold}}/T_{\text{hot}}$.

Solution (a) For an ideal gas the internal energy only depends on T and N so it is constant on the isothermal branch. Since $\Delta U_{AB} = 0$ then

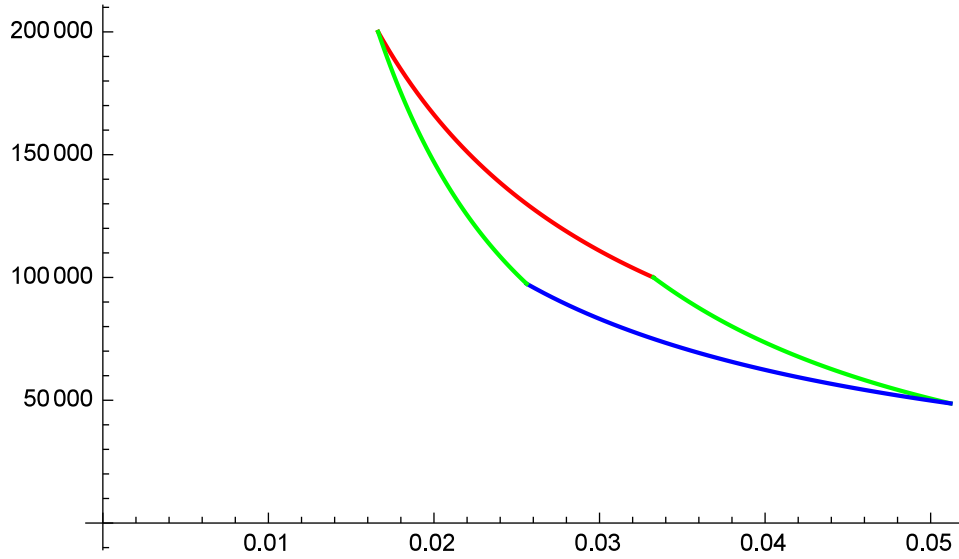$$Q_{AB} = -W_{AB} = \int_A^B pdV = \int_A^B \frac{NRT_{\text{hot}}}{V}dV = NRT_{\text{hot}}\ln(V_B/V_A)$$

Figure 8: Carnot engine cycle in $P - V$ diagram calculated in Mathematica.

which is Q_{hot}.

(b) By conservation of energy $\Delta U_{\circlearrowleft} = 0$ for a cycle so $Q_{\circlearrowleft} = -W_{\circlearrowleft} = \mathcal{W}_{\circlearrowleft}$. By definition, no heat is added or removed on the adiabatic branches so,

$$Q_{\circlearrowleft} = Q_{AB} + Q_{CD} = NRT_{\text{hot}} \ln(V_B/V_A) + NRT_{\text{cold}} \ln(V_D/V_C)$$

which equals $\mathcal{W}_{\circlearrowleft}$.

(c) From the definition of efficiency,

$$\eta = \frac{\mathcal{W}_{\circlearrowleft}}{Q_{\text{hot}}} = 1 + \frac{T_{\text{cold}} \ln(V_D/V_C)}{T_{\text{hot}} \ln(V_B/V_A)}$$

Since points B and C are on the same adiabatic branch $T_B V_B^{\gamma-1} = T_C V_C^{\gamma-1}$ so

$$V_B = V_C \left(\frac{T_C}{T_B}\right)^{\frac{1}{\gamma-1}} = V_C \left(\frac{T_{\text{cold}}}{T_{\text{hot}}}\right)^{\frac{1}{\gamma-1}}$$

Similarly,

$$V_A = V_D \left(\frac{T_D}{T_A}\right)^{\frac{1}{\gamma-1}} = V_D \left(\frac{T_{\text{cold}}}{T_{\text{hot}}}\right)^{\frac{1}{\gamma-1}}$$

Combining the above,

$$\frac{\ln(V_D/V_C)}{\ln(V_B/V_A)} = \frac{\ln(V_D/V_C)}{\ln(V_C/V_D)} = -1$$

Inserting this into our expression for η gives the desired result.

Example [From Kondepudi's book] (a) A Carnot refrigerator extracts 45.0 kJ from a cold reservoir and delivers 67.0 kJ of heat to a hot reservoir, which is at $T = 300$ K. What is the temperature of the cold reservoir? (b) What is the maximum work that a heat engine can deliver from 1000 Joules of heat supplied by a hot reservoir at 120 degrees Celsius; the cold reservoir is at 25 degrees Celsius.

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Solution (a) A Carnot refrigerator is a Carnot engine running backwards. Call A-D and C-B the adiabatic branches; the cold isothermal branch is D-C while the hot isothermal branch is B-A. For one full cycle we know that $\Delta S_{\circlearrowleft} = 0$ since the system returns to the same state so for this cycle,

$$\Delta S_{\circlearrowleft} = \Delta S_{AD} + \Delta S_{DC} + \Delta S_{CB} + \Delta S_{BA} = 0 + \frac{Q_{\text{hot}}}{T_{\text{cold}}} + 0 + \frac{Q_{\text{cold}}}{T_{\text{hot}}}$$

where Q_{hot} is the heat entering the system (the refrigerator) and Q_{cold} is the heat leaving the system. From this,

$$T_{\text{cold}} = -T_{\text{hot}} \frac{Q_{\text{cold}}}{Q_{\text{hot}}} = 201 \text{ K}$$

Remember that Q_{cold} is negative.

(b) From the definition of efficiency, $\eta = \mathcal{W}/Q_{\text{hot}}$, and the expression for Carnot efficiency we have,

$$\mathcal{W}_{\max} = \eta Q_{\text{hot}} = Q_{\text{hot}} \left(1 - \frac{T_{\text{hot}}}{T_{\text{cold}}} \right) = 242 \text{ Joules}$$

where Q_{hot} is the heat entering the system.

Example Consider a heat engine that is *not* a Carnot cycle but rather operates between constant pressures and volumes (i.e., the cycle is a rectangle in the $p - V$ diagram). The engine consisting of one mole of an ideal gas with $\gamma = 5/3$ operating between the high and low volumes of $V_{\text{high}} = 20$ liters and $V_{\text{low}} = 10$ liters; and the high and low pressures of $p_{\text{high}} = 8.0 \times 10^5$ Pa and $p_{\text{low}} = 4.0 \times 10^5$ Pa.

(a) Sketch the $p - V$ diagram for this engine.

(b) Find the work done, in Joules, per cycle of this engine.

(c) Find the high and low temperatures, T_{hot} and T_{cold}, in Kelvin. Mark the points where these occur on your $p - V$ diagram.

(d) Indicate on your $p - V$ diagram the parts of the cycle where heat energy is being added and the parts where heat energy is being removed from the system. (Hint: Remember that for an ideal gas $U(T)$).

(e) Find the heat added to the engine, in Joules, when the cycle goes from T_{cold} to T_{hot}.

(f) Find the efficiency of this engine and compare it with the efficiency of a Carnot engine operating between the same high and low temperatures.

Solution (a) See Figure 9.

(b) The work done by the engine is the area of the rectangle so

$$\mathcal{W}_{\circlearrowleft} = (p_{\text{high}} - p_{\text{low}})(V_{\text{high}} - V_{\text{low}}) = (4.0 \times 10^5 \text{ Pa})(1.0 \times 10^{-2} \text{ m}^3) = 4000 \text{ J}$$

You can also evaluate this by finding $\mathcal{W}_{\text{hot}} = 8000$ J and $\mathcal{W}_{\text{cold}} = -4000$ J.

(c) From ideal gas law,

$$T_{\text{hot}} = \frac{p_{\text{high}} V_{\text{high}}}{NR} = 1920 \text{ K} \qquad \text{and} \qquad T_{\text{cold}} = \frac{p_{\text{low}} V_{\text{low}}}{NR} = 481 \text{ K}$$

since $N = 1$ mole. These points are at the lower-left and upper-right corners of the rectangle.

(d) By the First Law $dQ = dU + d\mathcal{W}$ where $\mathcal{W}$ is the work done *by* the system. On branch AB the temperature is increasing (since pV increases) so U is increasing; the system is doing work since V is increasing. Thus $Q_{AB} > 0$. By similar arguments, $Q_{BC} < 0$, $Q_{CD} < 0$, and $Q_{DA} > 0$.
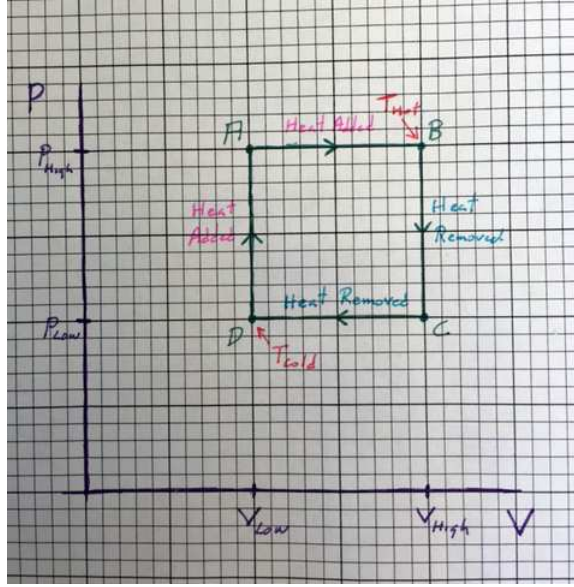
Figure 9: Rectangular engine cycle in $P - V$ diagram.

(e) By the First Law,

$$\Delta U_{DB} = Q_{DB} - \mathcal{W}_{DB} \qquad \text{or} \qquad Q_{DB} = \Delta U_{DA} + \Delta U_{AB} + \mathcal{W}_{DA} + \mathcal{W}_{AB}$$

Since $\gamma = C_p/C_V = 5/3$ and $C_p - C_V = NR$ for an ideal gas then $C_p = \frac{5}{2}NR$ and $C_V = \frac{3}{2}NR$. Using this we find

$$\Delta U_{DA} = C_V(T_A - T_D) = \frac{3}{2}(p_A V_A - p_D V_D) = 6000 \; J$$

and

$$\Delta U_{AB} = C_V(T_B - T_A) = \frac{3}{2}(p_B V_B - p_A V_A) = 12000 \; J$$

Finally, since $\mathcal{W}_{DA} = 0$ and $\mathcal{W}_{AB} = 8000$ J we have $Q_{DB} = 26000$ J.

(f) The efficiency of this engine is,

$$\eta = \frac{\mathcal{W}_{\circlearrowright}}{Q_{DB}} = 15.4\%$$

using the results from parts (b) and (e). A Carnot engine operating between the given high and low temperatures has efficiency,

$$\eta = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}} = 75\%$$

Example Consider a heat engine that is *not* a Carnot cycle but rather consists of a pair of adiabatic paths connected by a pair of isochoric (constant volume) paths. The engine consists of one mole of an ideal gas with $\gamma = 5/3$ operating between the high and low volumes of V_{high} and V_{low}.

(a) Sketch the $p - V$ diagram for this engine. Indicate on your sketch which branches are adiabatic and which ones are isochoric. Also indicate on which branches heat is added to the system and on which branches heat is removed from the system.

(b) Find the efficiency of this engine and show that it is $\eta = 75\%$ when $V_{\text{high}} = 8V_{\text{low}}$.

Solution (a) This type of heat engine is known as an Otto cycle (see Figure 8.1 on pg. 66). By definition no heat is added or removed on the adiabatic branches. On the upward isochoric branch, D-A, the pressure increases but the volume is fixed so internal energy increases but the system does no work. By First Law heat energy must be added to the system on this branch. By a similar argument heat is removed on the downward isochoric branch, B-C.

(b) The efficiency is

$$\eta = \frac{\mathcal{W}_{\circlearrowright}}{Q_{\text{hot}}} = 1 - \left| \frac{Q_{\text{cold}}}{Q_{\text{hot}}} \right| = 1 - \left| \frac{Q_{BC}}{Q_{DA}} \right|$$

where Q_{hot} is the heat added to the system and Q_{cold} is the heat removed from the system. Since $\gamma = C_p/C_V = 5/3$ and $C_p - C_V = NR$ for an ideal gas then $C_p = \frac{5}{2}NR$ and $C_V = \frac{3}{2}NR$. Using this and the fact that no work is done on these two branches we find

$$Q_{DA} = \Delta U_{DA} = C_V(T_A - T_D) = \frac{3}{2}(p_A V_A - p_D V_D)$$

and

$$Q_{BC} = \Delta U_{BC} = C_V(T_C - T_B) = \frac{3}{2}(p_C V_C - p_B V_B)$$

so

$$\eta = 1 - \left| \frac{Q_{BC}}{Q_{DA}} \right| = 1 - \left| \frac{(p_C V_C - p_B V_B)}{(p_A V_A - p_D V_D)} \right| = 1 - \left| \frac{(p_C - p_B)}{(p_A - p_D)} \right| \frac{V_B}{V_A}$$

To eliminate pressure from this expression we use the fact that on each adiabatic branch,

$$p_A V_A^\gamma = p_B V_B^\gamma \qquad \text{and} \qquad p_C V_C^\gamma = p_D V_D^\gamma$$

so

$$p_C - p_B = p_D(V_D/V_C)^\gamma - p_B = p_D(V_A/V_B)^\gamma - p_B \qquad \text{and} \qquad p_A - p_D = p_B(V_B/V_A)^\gamma - p_D$$

Put it all together,

$$\eta = 1 - \left| \frac{(p_C - p_B)}{(p_A - p_D)} \right| \frac{V_B}{V_A} = 1 - \left| \frac{p_D(V_A/V_B)^\gamma - p_B}{p_B(V_B/V_A)^\gamma - p_D} \right| \frac{V_B}{V_A} = 1 - \left(\frac{V_A}{V_B} \right)^{\gamma - 1}$$

For $\gamma = 5/3$ and $V_B = 8V_A$ we have $\eta = 1 - (1/8)^{2/3} = 3/4$.

Chapter 9: Open and Reactive Systems

Example A simple model for paramagnetism is a system consisting of $\mathcal{N}$ independent magnetic dipoles of mass m. Each dipole can be aligned either parallel or anti-parallel to an applied magnetic field. Call $\mathcal{N}_+$ the number that are parallel and $\mathcal{N}_-$ the number that are anti-parallel; note $\mathcal{N}_+ + \mathcal{N}_- = \mathcal{N}$. The internal energy of the system is,

$$U = (\mathcal{N}_- - \mathcal{N}_+)\epsilon$$

where ϵ is a dipole energy that depends on the dipole moment and the strength of the field.

(a) Find $\mathcal{N}_+$ and $\mathcal{N}_-$ in terms of U and $\mathcal{N}$.

(b) From statistical mechanics we find that the entropy is,

$$S(U, \mathcal{N}) = k_B \ln \left(\frac{\mathcal{N}!}{\mathcal{N}_+! \mathcal{N}_-!} \right) \approx k_B [\mathcal{N} \ln \mathcal{N} - \mathcal{N}_+ \ln \mathcal{N}_+ - \mathcal{N}_- \ln \mathcal{N}_-]$$

using Sterling's approximation for the factorial, $\ln x! \approx x \ln x - x$. In this paramagnetism model the volume is assumed constant. Use this result to find an expression for $T(U, M)$; remember that $M = m\mathcal{N}$. Hint: To simplify the algebra keep your expressions in terms of $\mathcal{N}_+(U, \mathcal{N})$ and $\mathcal{N}_-(U, \mathcal{N})$ until the final result.

(c) Find an expression for the chemical potential, $\mu(U, M)$; see hint for part (b).

Solution (a) Since $\mathcal{N} = \mathcal{N}_+ + \mathcal{N}_-$ then $\mathcal{N}_- = \mathcal{N} - \mathcal{N}_+$ so

$$U = (\mathcal{N}_- - \mathcal{N}_+)\epsilon = ((\mathcal{N} - \mathcal{N}_+) - \mathcal{N}_+)\epsilon = (\mathcal{N} - 2\mathcal{N}_+)\epsilon$$

Solve for $\mathcal{N}_+$ and $\mathcal{N}_+ = \frac{1}{2}(\mathcal{N} - U/\epsilon)$; similarly $\mathcal{N}_- = \frac{1}{2}(\mathcal{N} + U/\epsilon)$, or,

$$\mathcal{N}_+(U, M) = \frac{1}{2}\left(\frac{M}{m} - \frac{U}{\epsilon}\right) \qquad \text{and} \qquad \mathcal{N}_-(U, M) = \frac{1}{2}\left(\frac{M}{m} - \frac{U}{\epsilon}\right)$$

(b) Using the relation,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N$$

since $N = \mathcal{N}/N_A$ we have

$$\frac{1}{k_B T} = -(\ln \mathcal{N}_+ + 1)\left(\frac{\partial \mathcal{N}_+}{\partial U}\right)_{\mathcal{N}} - (\ln \mathcal{N}_- + 1)\left(\frac{\partial \mathcal{N}_-}{\partial U}\right)_{\mathcal{N}}$$

From part (a)

$$\left(\frac{\partial \mathcal{N}_+}{\partial U}\right)_{\mathcal{N}} = -\frac{1}{2\epsilon} \qquad \text{and} \qquad \left(\frac{\partial \mathcal{N}_-}{\partial U}\right)_{\mathcal{N}} = +\frac{1}{2\epsilon}$$

we have,

$$\frac{1}{k_B T} = \frac{1}{2\epsilon}\{\ln \mathcal{N}_+(U, \mathcal{N}) - \ln \mathcal{N}_-(U, \mathcal{N})\}$$

and solving for temperature,

$$T(U, M) = \frac{2\epsilon}{k_B} \frac{1}{\ln(\mathcal{N}_+/\mathcal{N}_-)}$$

Finish by inserting the expressions for $\mathcal{N}_+(U, M)$ and $\mathcal{N}_-(U, M)$. Notice that $T = 0$ when all the spins are parallel to the field ($\mathcal{N}_+ = \mathcal{N}$, $\mathcal{N}_- = 0$) and $T = \infty$ when there are equal numbers parallel and anti-parallel ($\mathcal{N}_+ = \mathcal{N}_- = \mathcal{N}/2$).

(c) Similar to part (b),

$$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial M}\right)_U = -\frac{1}{m}\left(\frac{\partial S}{\partial \mathcal{N}}\right)_U$$

since $M = m\mathcal{N}$. Evaluating the derivative,

$$\frac{m\mu}{k_B T} = -(\ln \mathcal{N} + 1) + (\ln \mathcal{N}_+ + 1)\left(\frac{\partial \mathcal{N}_+}{\partial \mathcal{N}}\right)_U + (\ln \mathcal{N}_- + 1)\left(\frac{\partial \mathcal{N}_-}{\partial \mathcal{N}}\right)_U$$

From part (a)

$$\left(\frac{\partial \mathcal{N}_+}{\partial \mathcal{N}}\right)_U = \frac{1}{2} \quad \text{and} \quad \left(\frac{\partial \mathcal{N}_-}{\partial \mathcal{N}}\right)_U = \frac{1}{2}$$

so

$$
\begin{aligned}
\mu(U, M) &= -\frac{k_B}{m}T(U, M)\left\{\ln \mathcal{N} - \frac{1}{2}\ln \mathcal{N}_+(U, \mathcal{N}) - \frac{1}{2}\ln \mathcal{N}_-(U, \mathcal{N})\right\} \\
&= \frac{k_B T}{2m}\ln\left(\frac{\mathcal{N}_+ \mathcal{N}_-}{\mathcal{N}^2}\right)
\end{aligned}
$$

Finish by inserting the expressions for $T(U, M)$, $\mathcal{N}_+(U, M)$, and $\mathcal{N}_-(U, M)$. One lesson to be learned from this problem is that the algebra can get very messy if you don't leave expressions in compact form.

Example (a) Find the rate of entropy production, $d_i S/dt$, for the set of elementary reactions,

$$
\begin{aligned}
\mathbb{X} + \mathbb{Y} &\rightleftharpoons 2\mathbb{Z} && \text{(Reaction 1)} \\
\mathbb{Z} + \mathbb{W} &\rightleftharpoons \mathbb{F} && \text{(Reaction 2)}
\end{aligned}
$$

in terms of ξ_1, ξ_2, T, and the chemical potentials of the five species.

(b) When species $\mathbb{Z}$ is neither produced nor consumed (i.e., it is at a steady state) the two elementary reaction can be written as a net reaction,

$$\mathbb{X} + \mathbb{Y} + 2\mathbb{W} \rightleftharpoons 2\mathbb{F}$$
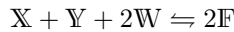
Show that in this case the rate of entropy production for the elementary reactions equals that of the net reaction,

$$\frac{d_i S_\Sigma}{dt} = \left(\frac{\mathcal{A}_\Sigma}{T}\right)\left(\frac{d\xi_\Sigma}{dt}\right)$$

where $\mathcal{A}_\Sigma$ and ξ_Σ are the chemical affinity and extent of the net reaction.

Solution (a) The total rate of entropy production is the sum of the rates of entropy production for each of the two elementary reactions, that is,

$$\frac{d_i S}{dt} = \frac{d_i S_1}{dt} + \frac{d_i S_2}{dt} = \frac{\mathcal{A}_1}{T}\frac{d\xi_1}{dt} + \frac{\mathcal{A}_2}{T}\frac{d\xi_2}{dt}$$

where the chemical affinities of the elementary reactions are,

$$\mathcal{A}_1 = \hat{\mu}_\mathbb{X} + \hat{\mu}_\mathbb{Y} - 2\hat{\mu}_\mathbb{Z} \quad \text{and} \quad \mathcal{A}_2 = \hat{\mu}_\mathbb{Z} + \hat{\mu}_\mathbb{W} - \hat{\mu}_\mathbb{F}$$

(b) If species $\mathbb{Z}$ is neither produced nor consumed then $dN_\mathbb{Z} = 0$. Since $dN_\mathbb{Z} = 2d\xi_1 - \xi_2$ this condition is,

$$\frac{d\xi_2}{dt} = 2\frac{d\xi_1}{dt}$$

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This just says that the first elementary reaction must occur at twice the rate of the other since the first produces one $\mathbb{Z}$ per reaction and the second consumes two $\mathbb{Z}$ per reaction. Using this condition in the result from part (a),

$$\frac{d_i S}{dt} = \frac{\mathcal{A}_1}{T}\frac{d\xi_1}{dt} + 2\frac{\mathcal{A}_2}{T}\frac{d\xi_1}{dt} = \frac{\mathcal{A}_\Sigma}{T}\frac{d\xi_1}{dt}$$
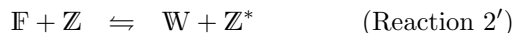
where

$$\mathcal{A}_\Sigma = \hat{\mu}_\mathbb{X} + \hat{\mu}_\mathbb{Y} + 2\hat{\mu}_\mathbb{W} - 2\hat{\mu}_\mathbb{F} = \mathcal{A}_1 + 2\mathcal{A}_2$$

is the affinity for the net reaction. Finally, $d\xi_1/dt = d\xi_\Sigma/dt$ since $dN_\mathbb{X} = d\xi_1 = d\xi_\Sigma$, which then gives the desired result.

Example Consider the uncoupled reactions,

$$\mathbb{Q} \;\rightleftharpoons\; \mathbb{X} + \mathbb{Y} \qquad \text{(Reaction 1)}$$
$$\mathbb{F} \;\rightleftharpoons\; \mathbb{W} \qquad \text{(Reaction 2)}$$

We also have the related coupled reactions,

$$\mathbb{X} + \mathbb{Z}^* \;\rightleftharpoons\; \mathbb{X}^* + \mathbb{Z} \qquad \text{(Reaction 1a}'\text{)}$$
$$\mathbb{X}^* + \mathbb{Y} \;\rightleftharpoons\; \mathbb{Q} \qquad \text{(Reaction 1b}'\text{)}$$
$$\mathbb{F} + \mathbb{Z} \;\rightleftharpoons\; \mathbb{W} + \mathbb{Z}^* \qquad \text{(Reaction 2}'\text{)}$$

where species $\mathbb{X}^*$ and $\mathbb{Z}^*$ are the "excited" versions of species $\mathbb{X}$ and $\mathbb{Z}$. Call $\Delta\hat{\mu}_\mathbb{X} = \hat{\mu}_\mathbb{X}^* - \hat{\mu}_\mathbb{X}$ and $\Delta\hat{\mu}_\mathbb{Z} = \hat{\mu}_\mathbb{Z}^* - \hat{\mu}_\mathbb{Z}$.

(a) Given the chemical potentials (in kJ/mol):

$$\hat{\mu}_\mathbb{X} = 3; \qquad \hat{\mu}_\mathbb{Y} = 2; \qquad \hat{\mu}_\mathbb{Q} = 9; \qquad \hat{\mu}_\mathbb{F} = 10; \qquad \hat{\mu}_\mathbb{W} = 1; \qquad \hat{\mu}_\mathbb{Z} = 4$$

Show that both uncoupled reactions have positive affinity so $\mathbb{Q}$ is consumed. Also show that for $\Delta\hat{\mu}_\mathbb{X} = 5$ and $\Delta\hat{\mu}_\mathbb{Z} = 7$ all three coupled reactions have positive affinity so $\mathbb{Q}$ is produced.

(b) Find a general expression for the upper and lower bounds for the values of $\Delta\hat{\mu}_\mathbb{X}$ and $\Delta\hat{\mu}_\mathbb{Z}$ for which all three coupled reactions have positive affinity. Express your result in terms of $\mathcal{A}_1$ and $\mathcal{A}_2$, the affinities of the uncoupled reactions.

Solution (a) The chemical affinities are,

$$\begin{aligned}
\mathcal{A}_1 &= \hat{\mu}_\mathbb{Q} - \hat{\mu}_\mathbb{X} - \hat{\mu}_\mathbb{Y} \\
\mathcal{A}_2 &= \hat{\mu}_\mathbb{F} - \hat{\mu}_\mathbb{W} \\
\mathcal{A}_{1a'} &= \hat{\mu}_\mathbb{X} + \hat{\mu}_{\mathbb{Z}^*} - \hat{\mu}_{\mathbb{X}^*} - \hat{\mu}_\mathbb{Z} \\
\mathcal{A}_{1b'} &= \hat{\mu}_{\mathbb{X}^*} + \hat{\mu}_\mathbb{Y} - \hat{\mu}_\mathbb{Q} \\
\mathcal{A}_{2'} &= \hat{\mu}_\mathbb{F} + \hat{\mu}_\mathbb{Z} - \hat{\mu}_\mathbb{W} - \hat{\mu}_{\mathbb{Z}^*}
\end{aligned}$$

For the values given, $\mathcal{A}_1 = 4$, $\mathcal{A}_2 = 9$, $\mathcal{A}_{1a'} = 2$, $\mathcal{A}_{1b'} = -\mathcal{A}_1 + \Delta\hat{\mu}_\mathbb{X} = 1$, and $\mathcal{A}_{2'} = \mathcal{A}_2 - \Delta\hat{\mu}_\mathbb{Z} = 2$.

(b) If $\mathcal{A}_{1a'} > 0$ then $(\hat{\mu}_{\mathbb{Z}^*} - \hat{\mu}_\mathbb{Z}) - (\hat{\mu}_{\mathbb{X}^*} - \hat{\mu}_\mathbb{X}) > 0$ so $\Delta\hat{\mu}_\mathbb{Z} > \Delta\hat{\mu}_\mathbb{X}$. If $\mathcal{A}_{1b'} > 0$ then $\hat{\mu}_{\mathbb{X}^*} + \hat{\mu}_\mathbb{Y} - \hat{\mu}_\mathbb{Q} > 0$ so $\hat{\mu}_{\mathbb{X}^*} - \hat{\mu}_\mathbb{X} > \hat{\mu}_\mathbb{Q} - \hat{\mu}_\mathbb{Y} - \hat{\mu}_\mathbb{X}$ or $\Delta\hat{\mu}_\mathbb{X} > \mathcal{A}_1$. If $\mathcal{A}_{2'} > 0$ then $\hat{\mu}_\mathbb{F} + \hat{\mu}_\mathbb{Z} - \hat{\mu}_\mathbb{W} - \hat{\mu}_{\mathbb{Z}^*} > 0$ or $\mathcal{A}_2 = \hat{\mu}_\mathbb{F} - \hat{\mu}_\mathbb{W} > \Delta\hat{\mu}_\mathbb{Z}$. In summary, we require that,

$$\begin{aligned}
\Delta\hat{\mu}_\mathbb{Z} &> \Delta\hat{\mu}_\mathbb{X} \\
\Delta\hat{\mu}_\mathbb{X} &> \mathcal{A}_1 \\
\mathcal{A}_2 &> \Delta\hat{\mu}_\mathbb{Z}
\end{aligned}$$

or

$$\mathcal{A}_2 > \Delta\hat{\mu}_\mathbb{Z} > \Delta\hat{\mu}_\mathbb{X} > \mathcal{A}_1$$

You can check that the values in part (a) satisfy this inequality.

Chapter 10: Second Law – Open & Reactive Systems

Example Show that for heat and mass flow in a heterogenous systems each of the thermodynamic forces and flows may be written as,

$$\mathcal{F}_{\mathcal{X}} = \left(\frac{\partial S_R}{\partial \mathcal{X}_R}\right)_{\{\mathcal{Y}_R\}} - \left(\frac{\partial S_L}{\partial \mathcal{X}_L}\right)_{\{\mathcal{Y}_L\}} \qquad \text{and} \qquad \mathcal{J}_{\mathcal{X}} = \left(\frac{d\mathcal{X}_R}{dt}\right)$$

where $\mathcal{X}$ is either U or M_k and $\{\mathcal{Y}\}$ is the set $\{U, V, \mathbf{M}\}$ but without $\mathcal{X}$. Consider the case of multiple species but without chemistry.

Solution Recall that from $dU = TdS - pdV + \sum_k \mu_k dM_k$ we have

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \sum_k \frac{\mu_k}{T}dM_k$$

so

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,\mathbf{M}} \qquad \text{and} \qquad \frac{\mu_i}{T} = -\left(\frac{\partial S}{\partial M_i}\right)_{U,V,\{M_{j \neq i}\}}$$

For $\mathcal{X} = U$,

$$\mathcal{F}_U = \left(\frac{\partial S_R}{\partial U_R}\right)_{V_R,\mathbf{M}_R} - \left(\frac{\partial S_L}{\partial U_L}\right)_{V_L,\mathbf{M}_L} = \frac{1}{T_R} - \frac{1}{T_L}$$

and

$$\mathcal{J}_U = \left(\frac{dU_R}{dt}\right) = \left(\frac{dU_\rightarrow}{dt}\right)$$

The demonstration for the mass fluxes is similar and the same result holds for systems that can exchange volume (see Example 7.4 on pg. 59).

Chapter 11: Phenomenological Laws

Example Consider a system with two thermodynamic forces, $\mathcal{F}_1$ and $\mathcal{F}_2$, with two corresponding thermodynamic flows, $\mathcal{J}_1$ and $\mathcal{J}_2$. For this system Onsager theory gives the rate of local entropy production as,

$$\sigma = \sum_{i=1}^{2} \mathcal{F}_i \mathcal{J}_i \qquad \text{and} \qquad \mathcal{J}_i = \sum_{j=1}^{2} L_{i,j} \mathcal{F}_j$$

Show that $\sigma \geq 0$ requires that the Onsager coefficients satisfy the relations,

$$L_{1,1} \geq 0, \qquad L_{2,2} \geq 0, \qquad \text{and} \qquad L_{1,1} L_{2,2} - L_{1,2}^2 \geq 0$$

Hint: Use the Onsager reciprocal relation $L_{1,2} = L_{2,1}$.

Solution We start by explicitly writing the two equations,

$$\begin{aligned}
\mathcal{J}_1 &= L_{1,1}\mathcal{F}_1 + L_{1,2}\mathcal{F}_2 \\
\mathcal{J}_2 &= L_{2,1}\mathcal{F}_1 + L_{2,2}\mathcal{F}_2
\end{aligned}$$

Use the second equation to write

$$\mathcal{F}_2 = \frac{1}{L_{2,2}}\mathcal{J}_2 - \frac{L_{2,1}}{L_{2,2}}\mathcal{F}_1$$

and eliminate $\mathcal{F}_2$ in the first equation and,

$$\mathcal{J}_1 = \left(L_{1,1} - \frac{L_{1,2}L_{2,1}}{L_{2,2}}\right)\mathcal{F}_1 + \frac{L_{1,2}}{L_{2,2}}\mathcal{J}_2$$

Inserting this into the expression for entropy production rate,

$$\begin{aligned}
\sigma &= \mathcal{J}_1 \mathcal{F}_1 + \mathcal{J}_2 \mathcal{F}_2 \\
&= \left(L_{1,1} - \frac{L_{1,2}L_{2,1}}{L_{2,2}}\right)\mathcal{F}_1^2 + \frac{L_{1,2}}{L_{2,2}}\mathcal{F}_1\mathcal{J}_2 + \frac{1}{L_{2,2}}\mathcal{J}_2^2 - \frac{L_{2,1}}{L_{2,2}}\mathcal{F}_1\mathcal{J}_2 \\
&= \left(L_{1,1} - \frac{L_{1,2}^2}{L_{2,2}}\right)\mathcal{F}_1^2 + \frac{1}{L_{2,2}}\mathcal{J}_2^2
\end{aligned}$$

where we eliminated terms using the Onsager reciprocity relation, $L_{1,2} = L_{2,1}$. Since $\sigma \geq 0$ for all possible values of $\mathcal{F}_1$ and $\mathcal{J}_2$ setting $\mathcal{F}_1 = 0$ tells us that $L_{2,2} \geq 0$. Similarly, setting $\mathcal{J}_2 = 0$ gives us that $L_{1,1}L_{2,2} - L_{1,2}^2 \geq 0$. Finally, the derivation above may be repeated switching the indices 1 and 2 and the resulting expression setting $\mathcal{F}_2 = 0$ gives $L_{1,1} \geq 0$.

Example Again, consider a system with two thermodynamic forces, $\mathcal{F}_1$ and $\mathcal{F}_2$, with two corresponding thermodynamic flows, $\mathcal{J}_1$ and $\mathcal{J}_2$. The pure resistance, $\mathcal{P}_1$, is defined as,

$$\mathcal{P}_1 = \frac{\mathcal{F}_1}{\mathcal{J}_1} \text{ when } \mathcal{J}_2 = 0$$

Find an expression for $\mathcal{P}_1$ in terms of $L_{1,1}$, $L_{2,2}$, $L_{1,2}$, and $L_{2,1}$.

Solution We start by explicitly writing the two equations,

$$\begin{aligned}
\mathcal{J}_1 &= L_{1,1}\mathcal{F}_1 + L_{1,2}\mathcal{F}_2 \\
\mathcal{J}_2 &= L_{2,1}\mathcal{F}_1 + L_{2,2}\mathcal{F}_2
\end{aligned}$$

When $\mathcal{J}_2 = 0$ we have

$$\mathcal{F}_2 = -\frac{L_{2,1}}{L_{2,2}}\mathcal{F}_1$$

Inserting this into the first equation,

$$\mathcal{J}_1 = L_{1,1}\mathcal{F}_1 + L_{1,2}\left(-\frac{L_{2,1}}{L_{2,2}}\mathcal{F}_1\right) = \left\{L_{1,1} - \frac{L_{1,2}L_{2,1}}{L_{2,2}}\right\}\mathcal{F}_1$$

so

$$\mathcal{P}_1 = \frac{\mathcal{F}_1}{\mathcal{J}_1} = \frac{L_{2,2}}{L_{1,1}L_{2,2} - L_{1,2}L_{2,1}} = \frac{L_{2,2}}{L_{1,1}L_{2,2} - L_{1,2}^2}$$

Note that from the previous example we know that $\mathcal{P}_1 \geq 0$; note that this is the same as $P_{1,1}$ (see the next example). When the cross-coefficients are small $\mathcal{P}_1 \approx 1/L_{1,1}$.

Example Again, consider a system with two thermodynamic forces, $\mathcal{F}_1$ and $\mathcal{F}_2$, with two corresponding thermodynamic flows, $\mathcal{J}_1$ and $\mathcal{J}_2$. We may use the Onsager resistance matrix, $P_{i,j}$, instead of the Onsager conductance matrix, $L_{i,j}$, and write,

$$\frac{d_i S}{dt} = \sum_{i=1}^{2} \mathcal{F}_i \mathcal{J}_i \qquad \text{and} \qquad \mathcal{F}_i = \sum_{j=1}^{2} P_{i,j} \mathcal{J}_j$$

Find expressions for $P_{1,1}$, $P_{2,2}$, $P_{1,2}$, and $P_{2,1}$ in terms of $L_{1,1}$, $L_{2,2}$, $L_{1,2}$, and $L_{2,1}$.

Solution My approach to this problem was to write the Onsager relations in matrix-vector form,

$$\left(\begin{array}{c} \mathcal{J}_1 \\ \mathcal{J}_2 \end{array}\right) = \left(\begin{array}{cc} L_{1,1} & L_{1,2} \\ L_{2,1} & L_{2,2} \end{array}\right)\left(\begin{array}{c} \mathcal{F}_1 \\ \mathcal{F}_2 \end{array}\right) \qquad \text{and} \qquad \left(\begin{array}{c} \mathcal{F}_1 \\ \mathcal{F}_2 \end{array}\right) = \left(\begin{array}{cc} P_{1,1} & P_{1,2} \\ P_{2,1} & P_{2,2} \end{array}\right)\left(\begin{array}{c} \mathcal{J}_1 \\ \mathcal{J}_2 \end{array}\right)$$

From this it's clear that the matrix $\mathbf{P} = \mathbf{L}^{-1}$, that is, it's the inverse of the matrix $\mathbf{L}$. The inverse of a 2-by-2 matrix is quite simple; the general result is,

$$\left(\begin{array}{cc} a & b \\ c & d \end{array}\right)^{-1} = \frac{1}{ad - bc}\left(\begin{array}{cc} d & -b \\ -c & a \end{array}\right)$$

so

$$\left(\begin{array}{cc} P_{1,1} & P_{1,2} \\ P_{2,1} & P_{2,2} \end{array}\right) = \frac{1}{L_{1,1}L_{2,2} - L_{1,2}L_{2,1}}\left(\begin{array}{cc} L_{2,2} & -L_{1,2} \\ -L_{2,1} & L_{1,1} \end{array}\right)$$

Using Onsager reciprocity we have,

$$P_{1,1} = \frac{L_{2,2}}{L_{1,1}L_{2,2} - L_{1,2}^2} \qquad P_{1,2} = P_{2,1} = -\frac{L_{1,2}}{L_{1,1}L_{2,2} - L_{1,2}^2} \qquad P_{2,2} = \frac{L_{1,1}}{L_{1,1}L_{2,2} - L_{1,2}^2}$$

As an alternative approach you may also obtain these results by setting up the problem as,

$$\left(\begin{array}{cc} L_{1,1} & L_{1,2} \\ L_{2,1} & L_{2,2} \end{array}\right)\left(\begin{array}{cc} P_{1,1} & P_{1,2} \\ P_{2,1} & P_{2,2} \end{array}\right) = \left(\begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array}\right)$$

and grinding out the solution of the resulting set of linear equations. There's four equations in four unknowns but you can immediately simplify one using Onsager reciprocity, $P_{1,2} = P_{2,1}$.

Chapter 12: Thermodynamic Potentials

Example (a) Starting from the definition $H = U + pV$ derive

$$dH = TdS + Vdp + \sum_k \mu_k dM_k$$

(b) Starting from the definition $G = U + pV - TS$ derive

$$dG = -SdT + Vdp + \sum_k \mu_k dM_k$$

(c) Show that for fixed S and p in a closed system we have $dH/dt = -TV \; d_iS/dt$.
(d) Show that for fixed T and p in a closed system we have $dG/dt = -TV \; d_iS/dt$.

Solution (a) From the definition $H = U + pV$ and the Gibbs equation,

$$
\begin{aligned}
dH & = dU + pdV + Vdp \\
& = (TdS - pdV + \sum_k \mu_k dM_k) + pdV + Vdp \\
& = TdS + Vdp + \sum_k \mu_k dM_k
\end{aligned}
$$

(b) We can the definition as $G = U + pV - TS = H - TS$ so,

$$
\begin{aligned}
dG & = dH - TdS - SdT \\
& = (TdS + Vdp + \sum_k \mu_k dM_k) - TdS - SdT \\
& = -SdT + Vdp + \sum_k \mu_k dM_k
\end{aligned}
$$

(c) From part (a) for fixed S and p we have $dH = \sum_k \mu_k dM_k$. Since in a closed system $d_eM_k = 0$ then $dH = \sum_k \mu_k d_iM_k = -Td_iS$ so,

$$\frac{d_iS}{dt} = -\frac{1}{T}\frac{dH}{dt}$$

(d) From part (b) for fixed T and p we have $dG = \sum_k \mu_k dM_k$. The rest of the derivation is the same as in part (c).

Example Obtain an expression for the Helmholtz free energy, $F(T, V, M)$, for a pure ideal gas.

Solution Fortunately for an ideal gas we already have expressions for internal energy and entropy in the desired variables,

$$U(T, V, M) = c_V MT$$

and

$$S(T, V, M) = M[s_0 + (k_B/m) \ln(V/M) + c_V \ln(T)]$$

we may immediately write,

$$F(T, V, M) = U(T, V, M) - TS(T, V, M) = MT[c_V - s_0 - (k_B/m) \ln(V/M) - c_V \ln(T)]$$

Example Consider the functions $f(x)$ and $g(w)$ which are related by the Legendre transformation,

$$g = f - xw \qquad w = \frac{df}{dx}$$

(a) Show that g is the y-intercept of the tangent line of the function $f(x)$.

(b) Create a graph that illustrates the result from part (a) for the function $f(x) = 2\exp(x/2)$ for the values $x = 0$, 1, and 2. Also compute w and $g(w)$ at these three values of x.

Solution (a) The slope of the tangent line of f at the point x is the derivative $w = df/dx$. This slope may also be written as,

$$w = \frac{\text{Rise}}{\text{Run}} = \frac{f(x) - g}{x - 0}$$

which gives the desired result after collecting terms.

(b) For the function $f(x) = 2\exp(x/2)$ we have,

$$w = \frac{df}{dx} = e^{x/2} \qquad \text{and} \qquad x = 2\ln w$$

so

$$g(w) = f(x(w)) - x(w)w = 2w - 2w\ln w = 2w(1 - \ln w)$$

The Mathematica script below produced Figure 10; the values are $w(x) = 1, \sqrt{e}, e$ and $g(w) = 2, \sqrt{e}, 0$.

```
f[x_]  := 2 Exp[x/2];
g[w_]  := 2 w (1 - Log[w]);
ww[x_]  := Exp[x/2];
xx[w_]  := 2 Log[w];
t0[x_]  := g[ww[0]]+ww[0] x;
t1[x_]  := g[ww[1]]+ww[1] x;
t2[x_]  := g[ww[2]]+ww[2] x;
wValues ={ww[0],ww[1],ww[2]}
gValues ={g[ww[0]],g[ww[1]],g[ww[2]]}
Plot[{f[x],t0[x],t1[x],t2[x]},{x,-1,4}]
```

Example (a) Show that for a pure substance,

$$\left(\frac{\partial \mu}{\partial p} \right)_T = \frac{V}{M}$$

Hint: Start by considering how G varies with p.

(b) Using the result from part (a) show that the chemical potential for a pure ideal gas can be written as,

$$\mu^{\text{ideal}}(T, p) = \mu^0(T) + \frac{k_B}{m} T \ln(p/p^0)$$

where $\mu_0(T) = \mu(T, p^0)$ and p^0 is a reference pressure.

(c) For the "hard" van der Waals gas the pressure is,
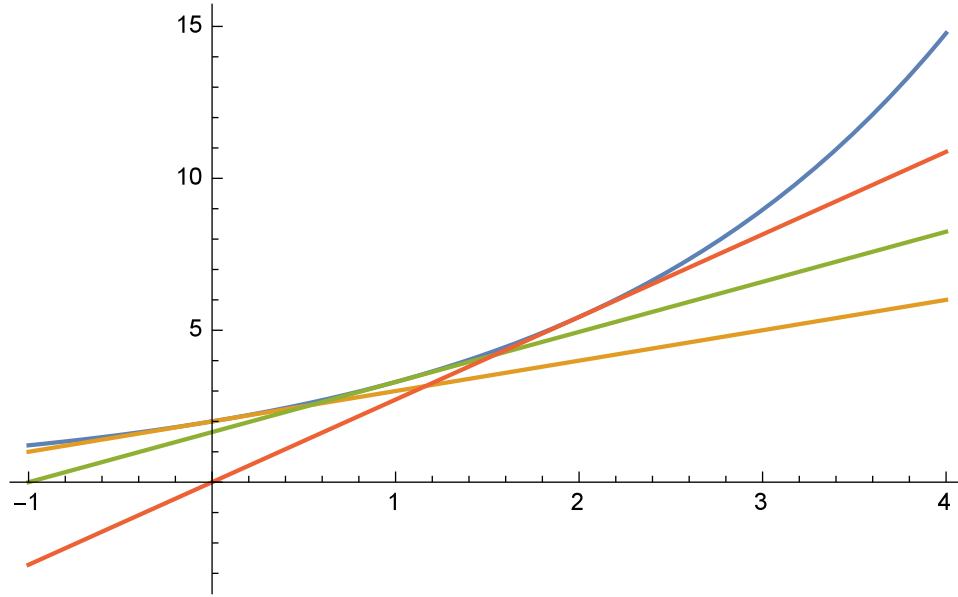
$$p = \frac{NRT}{V - Nb}$$

Figure 10: Tangent lines of $f(x)$ at various values of x.

where b is a positive constant. Show that the chemical potential for this gas can be written as,

$$\mu^{\mathrm{vdW}}(T,p) = \mu^{\mathrm{ideal}}(T,p) + \mathcal{A}(p - p_0)$$

and find the constant $\mathcal{A}$ in terms of b, m, and physical constants.

Solution (a) Using $dG = -SdT + Vdp + \sum_k \mu_k dM_k$, for a pure substance $dG = -SdT + Vdp + \mu dM$ so,

$$\left(\frac{\partial G}{\partial p}\right)_{T,M} = V$$

Since $G(T,p,M) = \mu(T,p)M$,

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \frac{V}{M}$$

Note that an alternative approach for solving this problem is to use the Gibbs-Duhem relation, which gives the answer by inspection.

(b) Using the ideal gas law with $M = m\mathrm{N_A}N$, $\mathrm{R} = \mathrm{k_B N_A}$,

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \frac{\mathrm{k_B}T}{mp}$$

Writing this as a differential equation in p,

$$\frac{d\mu}{dp} = \frac{\mathrm{k_B}T}{mp} \qquad (\text{Fixed } T)$$

so integrating both sides from p_0 to p for fixed T,

$$\mu(T,p) - \mu(T,p_0) = \frac{\mathrm{k_B}}{m}T(\ln(p) - \ln(p_0))$$

which completes the derivation after collecting terms.

(c) For the "hard" van der Waals gas, $V = NRT/p + bN$ so

$$\frac{d\mu}{dp} = \frac{V}{M} = \frac{k_{\mathrm{B}}T}{mp} + \frac{bN}{M} \qquad \text{(Fixed } T)$$

so after integrating we have the desired additional term with $\mathcal{A} = bN/M = b/m\mathrm{N_A}$.

Chapter 13: Thermodynamic Relations

Example For a pure closed system experiments indicated that the coefficient of thermal expansion, α, is of the form,

$$\alpha = \frac{1}{T + T_0}$$

where T_0 is a constant. Show that this implies that

$$\left(\frac{\partial C_p}{\partial p}\right)_{T,\mathbf{M}} = 0$$

Solution We first need to rearrange the derivatives (with $\mathbf{M}$ fixed everywhere) as,

$$
\begin{aligned}
\left(\frac{\partial C_p}{\partial p}\right)_T &= \left(\frac{\partial}{\partial p} T \left(\frac{\partial S}{\partial T}\right)_p\right)_T \\
&= T\frac{\partial^2 S}{\partial p \partial T} = T\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial p}\right)_T\right)_p
\end{aligned}
$$

Using the Maxwell relation,

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p = -V\alpha$$

then

$$
\begin{aligned}
\left(\frac{\partial C_p}{\partial p}\right)_T &= T\left(\frac{\partial}{\partial T}(-V\alpha)\right)_p \\
&= -VT\left(\frac{\partial \alpha}{\partial T}\right)_p - \alpha T\left(\frac{\partial V}{\partial T}\right)_p \\
&= -VT\left(\frac{\partial \alpha}{\partial T}\right)_p - \alpha T(\alpha V)
\end{aligned}
$$

Finally, we insert our expression for α,

$$
\begin{aligned}
\left(\frac{\partial C_p}{\partial p}\right)_T &= T\left(\frac{V}{(T+T_0)^2} - (1/(T+T_0))^2 V\right) \\
&= 0
\end{aligned}
$$

Example Experimental results for a pure system find the equation of state for pressure to be,

$$p(T, V, N) = \frac{ANT^3}{V}$$

where A is a known constant. Theoretical calculations indicate that internal energy for this system is

$$U(T, V, N) = BNT^a \ln(V/V_0) + f(T, N)$$

where V_0 is a constant and $f(T, N)$ is an unknown function. Determine the numerical value of a and find an expression for B in terms of the other quantities.

Solution Since we're given $U(T, V, N)$ and $p(T, V, N)$ we'll compare those two expressions using,

$$\left(\frac{\partial U}{\partial V}\right)_{T,\mathbf{M}} = T\left(\frac{\partial p}{\partial T}\right)_{V,\mathbf{M}} - p$$

We directly evaluate the left hand side,

$$\left(\frac{\partial U}{\partial V}\right)_{T,\mathbf{M}} = \frac{BNT^a}{V}$$

and for the right hand side we need,

$$\left(\frac{\partial p}{\partial T}\right)_{V,\mathbf{M}} = \frac{3ANT^2}{V}$$

Put it all together,

$$\frac{BNT^a}{V} = T\left\{\frac{3ANT^2}{V}\right\} - \frac{ANT^3}{V}$$

and comparing terms you see that $a = 3$ and $B = 2A$.

Example (a) Derive the *Gibbs-Helmholtz equation*,

$$\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_{p,\mathbf{M}} = -\frac{H}{T^2}$$

Hint: First show that $S = -(\partial G/\partial T)_{p,\mathbf{M}}$ then use the relation $G = H - TS$.
   (b) For a certain system the Gibbs free energy is,

$$G(T, p, \mathbf{M}) = aT + b + \frac{c}{T}$$

where the coefficients a, b, and c are functions of p and $\mathbf{M}$. Find $H(T, p, \mathbf{M})$ and $S(T, p, \mathbf{M})$.

Solution (a) Since $dG(p, T, \mathbf{M}) = V\,dp - S\,dT + \sum_i \mu_i dM_k$,

$$\left(\frac{\partial G}{\partial T}\right)_{p,\mathbf{M}} = -S$$

Inserting this into the relation $G = H - TS$ and collecting terms,

$$\frac{G}{T^2} - \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_{p,\mathbf{M}} = \frac{H}{T^2}$$

where I've divided through by T^2 in anticipation of the desired result. Noticing that

$$\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_{p,\mathbf{M}} = -\frac{G}{T^2} + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_{p,\mathbf{M}}$$

we arrive at the Gibbs-Helmholtz equation.
   (b) From the Gibbs-Helmholtz equation the enthalpy is,

$$H = -T^2\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_{p,\mathbf{M}} = -T^2\left(\frac{\partial}{\partial T}\right)_{p,\mathbf{M}}\left[a + \frac{b}{T} + \frac{c}{T^2}\right] = b + \frac{2c}{T}$$

For the entropy, since $G = H - TS$,

$$S = \frac{H - G}{T} = \frac{(b + \frac{2c}{T}) - (aT + b + \frac{c}{T})}{T} = -a + \frac{c}{T^2}$$

Note that you can also arrive at this result using

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,\mathbf{M}} = -\left(\frac{\partial}{\partial T}\right)_{p,\mathbf{M}} \left[aT + b + \frac{c}{T}\right] = -a + \frac{c}{T^2}$$

Example Express the rate of change of pressure when temperature changes adiabatically in terms of α and C_p. Take $\mathbf{M}$ as fixed; do *not* assume an ideal gas.

Solution The quantity we want to find is:

$$
\begin{aligned}
\left(\frac{\partial p}{\partial T}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_p && \text{(Using D3$'$)} \\
&= \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial S}{\partial T}\right)_p && \text{(Using M4)} \\
&= \left(\frac{1}{V\alpha}\right)\left(\frac{C_p}{T}\right) && \text{(Using definitions of } \alpha, C_p) \\
&= \frac{C_p}{TV\alpha}
\end{aligned}
$$

Chapter 14: Thermodynamic Fluctuations

No supplemental examples for this chapter.