

Chapter 6

Thermodynamic Driving Forces

1. One-dimensional lattice.

You have a one-dimensional lattice that contains N_A particles of type A and N_B particles of type B . They completely fill the lattice, so the number of sites is $N_A + N_B$.

- (a) Express the entropy $S(N_A, N_B)$ as a function of N_A and N_B .
- (b) Give the relationship between the chemical potential μ_A and the quantity $(\partial S / \partial N_A)_{N_B}$.
- (c) Express $\mu_A(N_A, N_B)$ as a function of N_A and N_B .

$$(a) \quad W(N_A, N_B) = \frac{(N_A + N_B)!}{N_A! N_B!},$$

$$S = k \ln W = k [(N_A + N_B) \ln(N_A + N_B) - N_A \ln N_A - N_B \ln N_B].$$

$$(b) \quad dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu_A}{T} dN_A - \frac{\mu_B}{T} dN_B,$$

$$\frac{\mu_A}{T} = - \left(\frac{\partial S}{\partial N_A} \right)_{N_B, U, V}.$$

$$(c) \quad \left(\frac{\partial S}{\partial N_A} \right)_{N_B} = k [\ln(N_A + N_B) + 1 - \ln N_A - 1] = -k \ln \left(\frac{N_A}{N_A + N_B} \right),$$

$$\mu_A = kT \ln \left(\frac{N_A}{N_A + N_B} \right) = kT \ln C,$$

where C is the mole fraction concentration of A 's in B 's.

(c)

$$\begin{aligned}\Delta S &= N_1 k \ln\left(\frac{V_2}{V_1}\right) + (N_2 - N_1)k \ln V_2 \\ &= k(N_1 \ln V_2 - N_1 \ln V_1 + N_2 \ln V_2 - N_1 \ln V_2) \\ &= k(N_2 \ln V_2 - N_1 \ln V_1).\end{aligned}$$

(d)

$$\begin{aligned}\Delta S &= (N_2 - N_1)k \ln V_1 + N_2 k \ln\left(\frac{V_2}{V_1}\right) \\ &= k(N_2 \ln V_2 - N_1 \ln V_1).\end{aligned}$$

4. Compute $\Delta S(V)$ for an ideal gas.

What is the entropy change if you double the volume from V to $2V$ in a quasi-static isothermal process at temperature T ?

$$\Delta S = S_2 - S_1 = Nk \ln\left(\frac{2V}{V}\right) = Nk \ln 2.$$

Chapter 7

The Logic of Thermodynamics

1. The work of compression.

One mole of a van der Waals gas is compressed quasi-statically and isothermally from volume V_1 to V_2 . For a van der Waals gas, the pressure is

$$p = \frac{RT}{V-b} - \frac{a}{V^2},$$

where a and b are material constants, V is the volume, and RT is the gas constant \times temperature.

- Write the expression for the work done.
- Is more or less work required than in the low-density limit than for an ideal gas? What about the high-density limit? Why?

(a) $w = - \int_{V_1}^{V_2} p_{\text{ext}} dV$. In a quasi-static process,

$$p_{\text{ext}} = p_{\text{gas}} = \frac{RT}{V-b} - \frac{a}{V^2},$$

$$w = \int_{V_1}^{V_2} \left[\left(\frac{-RT}{V-b} \right) + \left(\frac{a}{V^2} \right) \right] dV = -RT \ln \left(\frac{V_2-b}{V_1-b} \right) - a \left(\frac{1}{V_2} - \frac{1}{V_1} \right).$$

(b) For large volumes, the logarithm term is small and for, $V_2 < V_1$,

$$-a \left(\frac{1}{V_2} - \frac{1}{V_1} \right) < 0.$$

Therefore *less* work is required to compress a real gas. The van der Waals gas has internal attractive energy, which aids compression. On the other hand, when the

volumes are small (high densities), the logarithm term is dominant and the van der Waals gas has stronger repulsion; in that case, *more* work is required to compress it than an ideal gas.

2. Deriving the ideal gas law in two dimensions.

Molecules at low density on a surface, such as surfactants at an interface of air and water, often obey a two-dimensional equivalent of the ideal gas law. The two-dimensional equivalent of p is π , where π is a lateral two-dimensional pressure. A is area. Using

$$\pi = T \left(\frac{\partial S}{\partial A} \right)_N$$

and assuming no energetic interactions, derive the two-dimensional equivalent of the ideal gas law by using a lattice model in the low-density limit.

As in the three-dimensional problem, we consider the N molecules randomly distributed on a lattice of M sites. In this case, we use a two-dimensional lattice. There are M possible placements for the first particle, $M - 1$ possible placements for the second particle, $M - 2$ for the third, and so on. Therefore the number of arrangements, W , is

$$W = \frac{(M!)}{(M - N)!N!}.$$

We use the Boltzmann equation

$$S = k \ln W = k \ln \left[\frac{M!}{(M - N)!N!} \right]$$

and Stirling's approximation ($x! \approx (x/e)^x$) to get

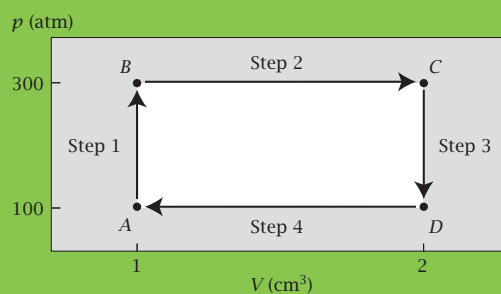
$$S = k \ln \left[\frac{M^M}{(M - N)^{M-N} N^N} \right] = -k \left[N \ln \left(\frac{N}{M} \right) + (M - N) \ln \left(\frac{M - N}{M} \right) \right].$$

Using the thermodynamic expression given in the problem,

$$\pi = T \left(\frac{\partial S}{\partial A} \right)_{U,N}; \quad \text{also,} \quad \left(\frac{\partial S}{\partial A} \right)_{U,N} = \left(\frac{\partial S}{\partial M} \right) \left(\frac{\partial M}{\partial A} \right),$$

6. The work in a thermodynamic cycle.

A thermodynamic cycle is a series of steps that ultimately returns to its beginning point. Compute the total work performed around the thermodynamic cycle of quasi-static processes in the figure below.



Using Equation (7.12) of the text, we have

$$\begin{aligned} W &= - \int_A^B p dV - \int_B^C p dV - \int_C^D p dV - \int_D^A p dV \\ &= 0 - (300 \text{ atm})(2 \text{ cm}^3 - 1 \text{ cm}^3) - 0 - (100 \text{ atm})(1 \text{ cm}^3 - 2 \text{ cm}^3) \\ &= -(200 \text{ atm cm}^3) \times (2.422 \times 10^{-2} \text{ cal cm}^{-3} \text{ atm}^{-1}) = -4.84 \text{ cal} \end{aligned}$$

Since steps 1 and 3 involve no volume change, there is no work performed during those steps.

7. Engine efficiencies.

Consider a Carnot engine that runs at $T_h = 380 \text{ K}$.

- Compute the efficiency if $T_c = 0^\circ\text{C} = 273 \text{ K}$.
- Compute the efficiency if $T_c = 50^\circ\text{C} = 323 \text{ K}$.

Equation (7.38) of the text gives

$$\eta = 1 - \frac{T_c}{T_h}.$$

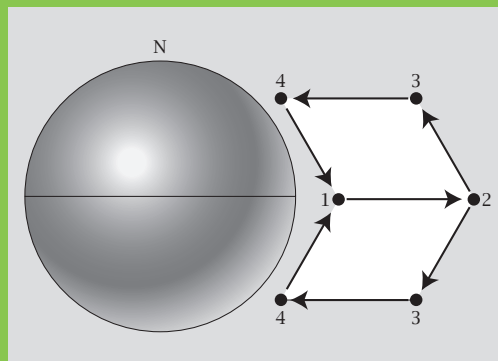
(a) $\eta = 1 - \frac{273}{380} = 28\%$ efficient.

(b) $\eta = 1 - \frac{323}{380} = 15\%$ efficient.

A big difference!

8. Hadley cycles—what powers the trade winds?

The Earth's trade winds arise from the differences in buoyancy between hot air and cold air. Air is heated at the Earth's surface near the equator (see (1) in the figure below), lowering its density; the air rises (2), pushing upper air away toward the Northern latitudes, where the air cools (3); then the air drops back down to Earth (4), pushing the cold surface air back toward the equator.



Consider an imaginary balloon containing 1 m^3 of an ideal gas.

- At $p = 1 \text{ atm}$ and $T = 300 \text{ K}$, what is the number of moles n of air contained in the balloon?
- If that balloon of n moles of air remains at $p = 1 \text{ atm}$ but is now heated to $T = 330 \text{ K}$, its volume increases. What is the new density $\rho = n/V$?
- Assuming no heat transfer, how high will the balloon in part (b) rise? Use Figure 10.2 in the text to make a rough guess. (Useful conversion: $1 \text{ atm} \approx 1 \text{ bar}$.)