# Chapter 14

# Open Systems

Following Gibbs, we consider neighboring containers of perfect gases in equilibrium with each other, as sketched in Fig. 14.1. The entropy of each gas is [see Eq. (8.27)]

$$\begin{aligned}\frac{S_i}{k} &= \beta U_i + \ln \chi_i(\beta) \\ &= N_i \left[ \frac{3}{2} + \frac{3}{2} \ln(2m\pi kT) + \ln V_i \right], \end{aligned} \tag{14.1}$$

in terms of the number of molecules in each box, $N_i$, the volume of each box, $V_i$, and the common temperature $T$. We suppose that the gases in the two boxes are identical, and have the same densities,

$$n = \frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N_1 + N_2}{V_1 + V_2}. \tag{14.2}$$

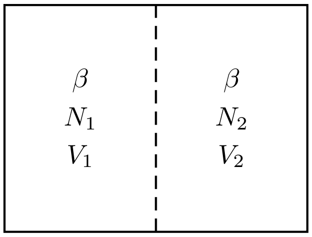

Figure 14.1: Two adjoining boxes contain ideal gases, both at the same temperature $T = 1/k\beta$. The number density of molecules in each box is assumed to be the same, $n = N_1/V_1 = N_2/V_2$, where $V_i$ is the volume of the $i$th box, containing $N_i$ molecules.

Now let the partition between the two boxes be removed; after the system again reaches equilibrium, the entropy of the combined system is

$$\frac{S}{k} = (N_1 + N_2)\left[\frac{3}{2} + \frac{3}{2}\ln(2m\pi kT) + \ln(V_1 + V_2)\right], \tag{14.3}$$

so the change in the entropy is

$$\begin{aligned}\frac{\Delta S}{k} &= \frac{S - S_1 - S_2}{k} = (N_1 + N_2)\ln(V_1 + V_2) - N_1 \ln V_1 - N_2 \ln V_2 \\ &= (N_1 + N_2)\ln(N_1 + N_2) - N_1 \ln N_1 - N_2 \ln N_2 > 0, \end{aligned} \tag{14.4}$$

since, for $y > 0$,

$$\frac{\partial}{\partial x}\left[(x + y)\ln(x + y) - x\ln x - y\ln y\right] = \ln(x + y) - \ln x > 0. \tag{14.5}$$

The result (14.4) is a sensible result for distinct gases, but if the gases are the same, this is peculiar—opening the partition should do nothing. This is the "Gibbs paradox." Gibbs decided that something had been left out of the definition of the entropy. For a *fixed* number $N$ of molecules, nothing is changed if we redefined the entropy by adding any function of $N$ to the entropy

$$\frac{S}{k} \to \frac{S}{k} - f(N) \tag{14.6}$$

A choice for $f$ that will solve the Gibbs paradox is

$$f(N) = N\ln N - \text{constant}\, N; \tag{14.7}$$

then in the above situation $\Delta S = 0$. If we further recall the Stirling approximation,

$$\ln N! \sim N\ln N - N, \tag{14.8}$$

we can adopt as the new definition of entropy

$$\frac{S_{\text{new}}}{k} = \frac{S_{\text{old}}}{k} - \ln N! \tag{14.9}$$

This suggests that we should replace the partition function by

$$\chi(\beta) \to \frac{\chi(\beta)}{N!}. \tag{14.10}$$

This is quite understandable—the molecules are identical, so permutations of them do not cause a real change in the system.

We remember that we could define the entropy in terms of the structure function by

$$\frac{S}{k} = \ln\Omega, \tag{14.11}$$

where for a two-component system

$$\begin{aligned}\Omega(E) &= \int dE_1\, \Omega_1(E_1)\Omega_2(E-E_1) \\ &\sim \Omega_1(E_{1,\max})\Omega_2(E-E_{1,\max})\Delta E_1,\end{aligned} \tag{14.12}$$

because, as we have seen many times, the function $\Omega_1$ is extremely sharply peaked. [See, for example, Eq. (10.19).] Then, of course,

$$\ln\Omega(E) = \ln\Omega_1(E_{1,\max}) + \ln\Omega_2(E-E_{1,\max}), \tag{14.13}$$

which implies that entropies are additive,

$$S = S_1 + S_2, \tag{14.14}$$

because $\ln\Delta E_1$ is negligible for large $N$.

Now what happens to the convolution law for open systems when the number of molecules can be changed? In the situation shown in Fig. 14.1, before the partition between the two boxes is removed, let the structure function for one molecule in the $i$th box be $\omega_i$, so the structure function for the $i$th box is

$$\Omega_i(E_i, N_i) = \int \delta(E_i - \sum_\gamma \varepsilon_\gamma) \prod_{\gamma=1}^{N_i} \omega_i(\varepsilon_\gamma)\, d\epsilon_\gamma \tag{14.15}$$

[this is just Eq. (9.4)], where the $\varepsilon_\gamma$s are the energies of the individual molecules. Now because the structure function for a single molecule is proportional to the volume [Eq. (9.32)], we see that when the partition is removed, the structure function for one molecule is

$$\omega(E) = \omega_1(E) + \omega_2(E), \tag{14.16}$$

and so the structure function for the combined system is ($E = E_1 + E_2$, $N = N_1 + N_2$)

$$\begin{aligned}\Omega(E,N) &= \int \delta(E - \sum_\gamma \varepsilon_\gamma) \prod_{\gamma=1}^{N} [\omega_1(\varepsilon_\gamma) + \omega_2(\varepsilon_\gamma)]\, d\varepsilon_\gamma \\ &= \sum_{N_1'=0}^{N} \int \delta\left(E - \sum_{\gamma=1}^{N_1'} \varepsilon_\gamma - \sum_{\gamma=N_1'+1}^{N} \varepsilon_\gamma\right) \prod_\gamma d\varepsilon_\gamma \\ &\quad \times \binom{N}{N_1'} \prod_{\gamma=1}^{N_1'} \omega_1(\varepsilon_\gamma) \prod_{\gamma=N_1'+1}^{N} \omega_2(\varepsilon_\gamma) \\ &= \sum_{N_1'=0}^{N} \binom{N}{N_1'} \int dE_1\, dE_2\, \delta(E - E_1 - E_2) \prod_\gamma d\varepsilon_\gamma\, \delta(E_1 - \sum_{\gamma=1}^{N_1'} \varepsilon_\gamma)\end{aligned}$$

$$\times\delta(E_2-\sum_{\gamma=N_1'+1}^{N}\varepsilon_\gamma)\prod_{\gamma=1}^{N_1'}\omega_1(\varepsilon_\gamma)\prod_{\gamma=N_1'+1}^{N}\omega_2(\varepsilon_\gamma)$$

$$=\sum_{N_1'=1}^{N}\binom{N}{N_1'}\int dE_1\,dE_2\,\delta(E-E_1-E_2)\Omega_1(E_1,N_1')\Omega_2(E_2,N-N_1'), \tag{14.17}$$

or

$$\frac{\Omega(E,N)}{N!}=\sum_{N_1'=1}^{N}\int dE_1\frac{\Omega_1(E_1,N_1')}{N_1'!}\frac{\Omega_2(E-E_1,N-N_1')}{(N-N_1')!} \tag{14.18}$$

This replaces the previous convolution law. This is understandable because $\Omega(E,N)/N!$ is the number of states with $N$ molecules having energy between $E$ and $E+dE$. The formula simply adds up all partitions of $E$ and $N$ between the two volumes.

Again, for large systems, thes functions are extremely peaked. We must find the maximum of

$$\frac{\Omega(E,N)}{N!}\sim\frac{\Omega_1(E_1,N_1)}{N_1!}\frac{\Omega_1(E_2,N_2)}{N_2!}\Delta E\Delta N, \tag{14.19}$$

where $E_2=E-E_1$ and $N_2=N-N_1$, and $E_1$ and $N_1$ are the extremum values. The extremum conditions are two:

$$\frac{\partial}{\partial E_1}\ln\frac{\Omega_1}{N_1!}=\frac{\partial}{\partial E_2}\ln\frac{\Omega_2}{N_2!}, \tag{14.20}$$

$$\frac{\partial}{\partial N_1}\ln\frac{\Omega_1}{N_1!}=\frac{\partial}{\partial N_2}\ln\frac{\Omega_2}{N_2!}. \tag{14.21}$$

Taking as our new definition of entropy,

$$\frac{S}{k}=\ln\frac{\Omega(E,N)}{N!}, \tag{14.22}$$

where [Eq. (8.15)]

$$\frac{\partial S}{\partial E}=k\beta=\frac{1}{T}, \tag{14.23}$$

Eq. (14.20) simply says that the two subsystems have the same temperature. For an ideal gas, because, from Eq. (14.1),

$$\ln\Omega-\ln N!\sim N\left(\frac{5}{2}+\frac{3}{2}\ln 2m\pi kT-\ln n\right), \tag{14.24}$$

where $n=N/V$, Eq. (14.21) says that the densities are equal,

$$n_1=n_2. \tag{14.25}$$

More generally, thermodynamically, when $N$, the number of particles, is a variable, we write the 1st law as

$$dU = \delta Q - \delta W + \mu\, dN = T\, dS - p\, dV + \mu\, dN, \tag{14.26}$$

where $\mu$ is called the chemical potential. We take this equation as defining the entropy, as a function of three extrinsic variables, $S(U, V, N)$:

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T}, \quad \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{p}{T}, \tag{14.27}$$

so that Eq. (14.21) demands the equality of chemical potentials.

Let us digress to discuss the chemical potential thermodynamically. We can define the Helmholtz free energy as before

$$F = U - TS, \tag{14.28}$$

so the first law says

$$dF = -S\, dT - p\, dV + \mu\, dN, \tag{14.29}$$

so we regard the Helmholtz free energy as a function of two extrinsic variables and one intrinsic variable, $F(T, V, N)$:

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S, \quad \left(\frac{\partial F}{\partial V}\right)_{T,N} = -p, \quad \left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu. \tag{14.30}$$

We now define the *Gibbs free energy* by

$$G = F + pV, \tag{14.31}$$

which, because of

$$dG = -S\, dT + V\, dp + \mu\, dN, \tag{14.32}$$

is to be regarded as a function of one extrinsic variable and two intrinsic ones, $G(T, p, N)$:

$$\left(\frac{\partial G}{\partial T}\right)_{p,N} = -S, \quad \left(\frac{\partial G}{\partial p}\right)_{T,N} = V, \quad \left(\frac{\partial G}{\partial N}\right)_{T,p} = \mu. \tag{14.33}$$

Consider a *homogeneous* system, that is, one for which

$$G(T, p, \lambda N) = \lambda G(T, p, N). \tag{14.34}$$

Then

$$N\frac{\partial G}{\partial N} = G, \tag{14.35}$$

which implies that

$$\mu = \frac{G}{N}, \tag{14.36}$$

that is, the chemical potential is the Gibbs free energy per particle. Then when we combine Eq. (14.32) with

$$dG = d(\mu N) = N\,d\mu + \mu\,dN, \tag{14.37}$$

we see that $\mu(T,p)$ satisfies

$$\left(\frac{\partial\mu}{\partial p}\right)_T = \frac{V}{N} = \frac{1}{n}, \quad \left(\frac{\partial\mu}{\partial T}\right)_p = -\frac{S}{N}, \tag{14.38}$$

the specific volume and the entropy per particle, respectively..

Check this for an ideal gas, where

$$\begin{aligned} S &= kN\left(\frac{5}{2} + \frac{3}{2}\ln 2\pi m\frac{U}{3N/2} - \ln\frac{N}{V}\right) \\ &= kN\left(\frac{5}{2} + \frac{3}{2}\ln\frac{4}{3}\pi m U - \frac{5}{2}\ln N + \ln V\right), \end{aligned} \tag{14.39}$$

so

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{3}{2}\frac{kN}{U} = \frac{1}{T}, \tag{14.40}$$

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} = \frac{S}{N} - \frac{5}{2}k = -\frac{\mu(T,p)}{T}, \tag{14.41}$$

where

$$\mu(T,p) = kT\left(\ln p - \frac{5}{2}\ln kT - \frac{3}{2}\ln 2\pi m\right). \tag{14.42}$$

Indeed we see

$$\left(\frac{\partial\mu}{\partial p}\right)_T = \frac{kT}{p} = \frac{V}{N}, \tag{14.43}$$

$$\left(\frac{\partial\mu}{\partial T}\right)_p = \frac{\mu}{T} - \frac{5}{2}k = -\frac{S}{N}. \tag{14.44}$$

## 14.1 Thermodynamic signficance of free energy

Let us consider the thermodynamic meaning of the two free energies, $F$ and $G$, for processes in which $N$ is constant. Because then

$$dF = -S\,dT - p\,dV, \tag{14.45}$$

$dF = 0$ for processes in which $T$ and $V$ are constant, or the Helmholtz free energy is an extremum (actually a minimum) for equilibrium processes in which there is no change in the temperature and volume. On the other hand,

$$dG = -S\,dT + V\,dp, \tag{14.46}$$

so $dG = 0$ for processes in which $T$ and $p$ are constant. The Gibbs free energy is an extremum (minimum) for equilibrium processes in which the temperature and pressure do not change.

For irreversible processes, the heat input is bounded above:

$$\delta Q < T\,dS, \tag{14.47}$$

so

$$dU = \delta Q - p\,dV < T\,dS - p\,dV, \tag{14.48}$$

and therefore

$$dF = dU - d(TS) < -S\,dT - p\,dV, \tag{14.49}$$

so if $dT = dV = 0$, $dF < 0$. Therefore, *an irreversible process occurring at constant temperature and volume is accompanied by a decrease in the Helmholtz free energy.* Similarly,

$$dG = dF + d(pV) < -S\,dT + V\,dp, \tag{14.50}$$

so if $dT = dp = 0$, $dG < 0$, or *an irreversible process occurring at constant temperature and pressure is accompanied by a decrease in the Gibbs free energy.*

## 14.2 System composed of two distinct gases

Finally, consider a system composed of two gases, $a$ and $b$. It is easy to prove that the composition law is

$$\begin{aligned}\Omega(E, N_a, N_b) = \sum_{N_{a1},N_{b1}} \binom{N_a}{N_{a1}} \binom{N_b}{N_{b1}} \int dE_1\, \Omega_1(E_1, N_{a1}, N_{b1}) \\ \times\Omega_2(E - E_1, N_a - N_{a1}, N_b - N_{b1}).\end{aligned} \tag{14.51}$$

Thus, the simple composition law is for

$$\frac{\Omega(E, N_a, N_b)}{N_a!N_b!}. \tag{14.52}$$

The Gibbs paradox is resolved by using

$$S = k \ln \left[\frac{\Omega(E, N_a, N_b)}{N_a!N_b!}\right]. \tag{14.53}$$

In particular, when different gases are mixed, the change in the entropy is just that seen in Eq. (14.4)

$$\frac{\Delta S}{k} = (N_a + N_b)\ln(N_a + N_b) - N_a \ln N_a - N_b \ln N_b. \tag{14.54}$$