CHAPTER 7
THE GIBBS MIXING PARADOX

In 1875 Willard Gibbs published his landmark paper "On the Equilibrium of Heterogeneous Substances". In this paper he determined the properties of an ideal gas mixture beginning with a definition relating the chemical potential of a component in the mixture, μ_i, to its partial pressure, p_i.

$$\mu_i = \mu_i^o + RT \ln p_i \qquad \textbf{(7-1)}$$

where μ_i° is a function only of temperature. This defining equation was to be justified by the validity of the "properties which may be deduced from it". These properties were:

(a) the equation of state
(b) the equilibrium constant for a gas-phase chemical reaction
(c) the properties of mixtures

Gibbs showed the equation of state for the ideal gas mixture to be

$$PV = RT \sum n_i \qquad \textbf{(7-2)}$$

which is the same equation that applies to the individual gases.

He then used available literature data for equilibrium compositions for the reaction

$$N_2O_4(g) \; = \; 2\, NO_2(g)$$

to demonstrate the constancy of the equilibrium constant.

7.1 THE PARADOX

In applying Eq. (7-1), Gibbs found the enthalpy and the volume of an ideal gas mixture to be the sum of the properties that the individual gases would exhibit at the conditions of the mixture. This leads to zero heat of mixing and zero volume change on mixing — a result verified by experience. However, when the entropy change is calculated for an isothermal, isobaric mixing process, the result is the now-familiar expression

$$\Delta s = -R \sum y_i \ln y_i \qquad \textbf{(7-3)}$$

The validity of Eq. (7-1) had been firmly established, but Gibbs was not comfortable with the expression for the entropy of mixing and his deliberations over this result have come to be known as the Gibbs mixing paradox.

According to Eq. (7-3), the entropy change on mixing equimolar quantities of two gases is

$$\Delta s = R \ln 2$$

a result that is seen to be independent of the nature of the gases. Gibbs was concerned about the "degree of dissimilarity" between the two gases for he had expected the entropy of mixing to depend on this factor. Instead he saw that as long as there is some dissimilarity, the entropy of mixing is $R\ln 2$, but when the "degree of dissimilarity" becomes zero (mixing the same gas), the entropy change is zero. Thus, the entropy of mixing depends not on the "degree of dissimilarity" but only on whether any dissimilarity exists. It is this either-or situation which constitutes the Gibbs mixing paradox. As we have seen, the paradox arises out of classical thermodynamics and does not require a statistical or molecular kinetic context. Several attempts have been made to resolve the paradox with the help of either quantum statistical mechanics or information theory. All have been evaluated by Denbigh and Denbigh[1] and found wanting.

The usual gaseous mixing process is carried out with no recovery of work and because the heat of mixing is zero, there is no exchange of heat with the surroundings. In fact, there is no observable change to indicate that the process occurred. Thus, without employing some method of chemical analysis, an observer could not distinguish between the mixing of the same gas and the mixing of different gases although an entropy change occurs in the latter case but not the former.

Equation (7-3) which gives the entropy of mixing was determined in an indirect but rigorous thermodynamic manner from Eq. (7-1) which seems to be amply justified. Still, we have seen that this quantity exhibits unexpected

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[1] K.G. Denbigh and J.S. Denbigh, *Entropy in Relation to Incomplete Knowledge*, Cambridge University Press, Cambridge, 1985.

behavior and further, because we can not execute a reversible process, direct experimental determination is not possible.[2]

7.2 AN IDEALIZED MIXING PROCESS

The reversible mixing of two gases, *A* and *B*, can be visualized with the aid of Fig. 7-1. The device is a cylinder fitted with two pistons: piston 1 is permeable only to gas *A* and piston 2 is permeable only to gas *B*. Figure 7-1a shows the original unmixed state, Fig. 7-1b an intermediate state, and Fig. 7-1c the final mixed state. The pressure exerted by *B* is the same on both sides of piston 2 and thus the movement of this piston to the right results in an expansion of gas *A* as its accessible volume, the total volume to the left of piston 2, increases. Similarly, the movement of piston 1 allows gas *B* to expand. The process is carried out reversibly and isothermally and the work from expanding gas *A* is

$$W_A = -\int P\,dV = -n_A R T \int_{V_A}^{V_A+V_B} \frac{dV}{V} \qquad \textbf{(7-4)}$$

Because ΔU is zero for this isothermal process, the first law requires $Q = -W$ and the entropy change is

$$\Delta S_A = \frac{Q_A}{T} = -\frac{W_A}{T} = n_A R \ln \frac{V_A+V_B}{V_A} \qquad \textbf{(7-5)}$$

A similar expression obtains for *B* and the entropy of mixing is

$$\Delta S = \Delta S_A + \Delta S_B = R\,[\, n_A \ln \frac{V_A+V_B}{V_A} + n_B \ln \frac{V_A+V_B}{V_B}\,] \qquad \textbf{(7-6)}$$

For the special case of mixing one half mol of each gas ($V_A = V_B$) we obtain $\Delta s = R\ln 2$. If the gases *A* and *B* were identical, the pistons would be identical and their movement would not affect the gas, therefore, no work could be obtained.

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[2] Indirect determinations of the entropy of mixing gases by means of galvanic cells agree with Eq. (7-3). R.A. Rapp and D.A. Shores, "Galvanic Cells for Thermodynamic (Equilibrium) Measurements", in *Physicochemical Measurements in Metals Research*, R.A. Rapp ed., Vol IV part 2, p. 156, Interscience, 1970.

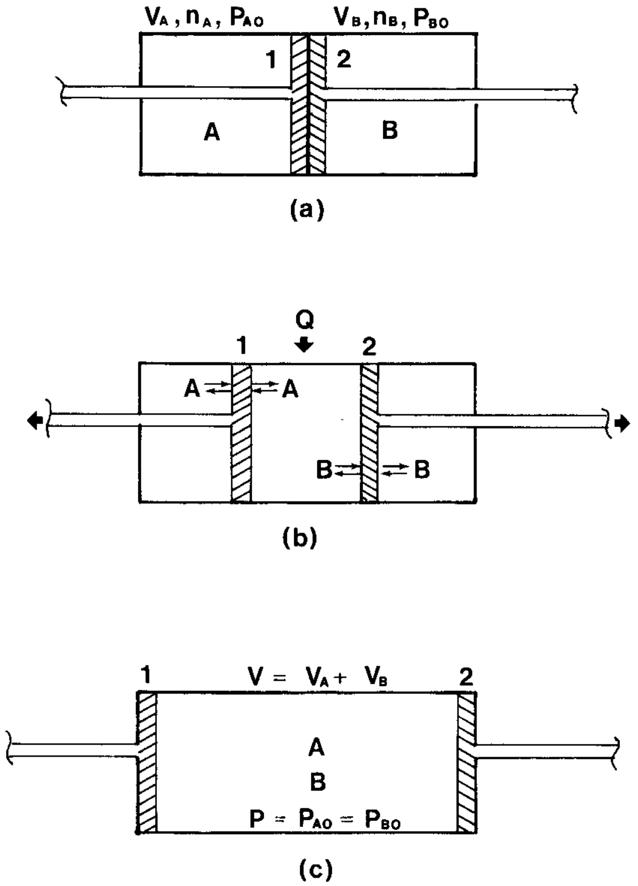

Figure 7-1. An idealized mixing process.

This idealized mixing process allows us to visualize the entropy of mixing in terms of a reversible heat effect in accordance with the definition of entropy. The result, Eq. (7-6), is easily reduced to Eq. (7-3). The either-or character of the entropy of mixing now can be associated with the either-or character of the semipermeable membranes which must be selected on the basis of "dissimilarities" of the gases.

The concept of a semipermeable barrier undoubtedly comes from experience with osmosis where membranes can be found that will pass water but not solute molecules. It is also known that palladium foil is permeable only to hydrogen gas. In these cases it appears that the membrane is permeable only to the smaller or uncharged species, however, no membrane is known to be permeable only to the larger or charged species. While membrane separation is employed commercially for the separation of certain gas mixtures, the membrane is permeable to both species and the separation depends on a difference in the rates of diffusion through the membrane. Although the idealization of complementary semipermeable membranes seems more remote than the usual idealizations such as adiabatic or frictionless processes which could be closely approached, it is useful and it yields the correct entropy of mixing. Further, it allows us to associate work with mixing and separation processes.

7.3 GIBBS' "VACUUM PRINCIPLE"

In commenting on the various derived properties of an ideal gas mixture, Gibbs observed that "every gas is a vacuum to every other gas". This is most clearly seen for the equation of state where the "vacuum principle" leads to the additivity of partial pressures as manifested by Dalton's law and zero volume change on mixing. It also accounts for zero heat of mixing. It would explain the non-dependence of the entropy of mixing on the "degree of dissimilarity" but it suggests that this entropy change should be found on mixing portions of the same gas. The vacuum principle simply offers another means of determining the properties of an ideal gas mixture. It does not provide a resolution of the Gibbs mixing paradox, however, it does permit a rephrasing. The question now is *Why is every gas a vacuum to every other gas except itself? Why should it matter to the molecules of portion A whether the commingling molecules of portion B are the same or dissimilar?* We have seen that for the energy and volume it doesn't matter.

7.4 THE MICROSCOPIC VIEW

In Chap. 2 we saw that a "naive" approach resulted in an entropy change of $R\ln 2$ for the mixing of two ½-mol quantities of the same gas. To obtain the correct result of zero it was necessary to make the *ad hoc* correction of dividing the naive partition function by $N!$. The justification for this correction was the indistinguishability of particles. This correction is unnecessary when the naive approach is applied to the mixing of different gases as both the naive and corrected approach yield the same entropy of mixing.[3]

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[3] See Appendix 7A for details

For the naive approach we see that the same volume, energy, and entropy changes are obtained for the mixing of two portions of gas regardless of identity. Every gas is indeed a vacuum to every other gas, including itself. The reason for this is that the quantum energy levels of a particle depend on its mass and the volume of the container.[4] And when two gases are mixed the set of energies[5] accessible to each species changes, but this change depends only on the volume change and is independent of species identity. Thus, from a "particle's-eye" view the naive approach seems reasonable.

7.5 PRACTICAL CONSIDERATIONS

As the concept of entropy arose from considerations of heat and work, the only unambiguous interpretation is practical — the total entropy change measures the deviation of a process from the reversible ideal. The total entropy change is zero for a reversible process and positive for an irreversible process. Consistent with its origins, entropy is intimately associated with the efficiency of processes. For a steady-state process that exchanges heat with the surroundings at T_0, a combination of the first and second law statements yields the total reversible work[6]

$$W_{rev} = \Delta H - T_0 \Delta S$$

The right-hand side of this equation is also known as the availability change, or exergy.

The idealized mixing process shows that work could be obtained, or that work is required to separate a mixture. Because the enthalpy change is zero, the availability change, or the reversible work is $-T_0\Delta S$ for the mixing of ideal gases and $T_0\Delta S$ for their separation. The concept of complementary semipermeable membranes provides insight into why this work, or the entropy of mixing, is independent of the "degree of dissimilarity" between the gases and also why no work is involved in mixing the same gas. This seems to be as close as we can

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[4] See Eq. (2-1)

[5] For a monatomic gas, there is only kinetic energy.

[6] For details see Sec. 14-2 of this textbook.

come to resolving the Gibbs mixing paradox. As long as there is any degree of dissimilarity, there exists, at least in principle, a complementary membrane pair which would allow reversible mixing or separation with work and heat effects(entropy changes) independent of the degree of dissimilarity. As we have seen, this explanation is based on the original macroscopic interpretation of entropy which arose from considerations of process efficiency.

It is the economic or utilitarian aspect of the situation, the work of separation, that forces the inclusion of $N!$ into the naive microscopic description of Sec.2.3.1. The reversal of the mixing process requires separational work when the gases are different. However, we have neither the need nor the ability to exactly reverse the mixing of portions of the same gas and therefore need expend no separational work. Because the minimum work of separation is $T_0\Delta S$ for ideal gas mixtures, there must never be an entropy change on mixing the same gas. The microscopic description is brought into conformance with the macroscopic situation by requiring indistinguishability of particles. Thus, a utilitarian consideration, human in origin, requires the insertion of a logical (or human-scented) term into the microscopic model.

APPENDIX 7A
THE MICROSCOPIC ENTROPY OF MIXING

The entropy of mixing *A* and *B* can be written

$$\Delta S = S_{AB} - S_A - S_B \tag{7-7}$$

with the separate entropy terms obtained from the partition function via Eq. (2-9)

$$S = k \ln Z + k\,T\left(\frac{\partial \ln Z}{\partial T}\right)_V \tag{2-9}$$

The Naive Approach

For pure gases we have seen that because the energy of the assembly is simply the sum of the particle energies, the assembly partition function can be written as the product of the particle partition functions

$$Z = z^N = V^N\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}}$$

There is no interaction energy between the *A* and *B* particles and the energy of the assembly is the sum of the particle energies. As shown in Appendix 2C the independence of the energies results in the product of partition functions and we write for the *A*-*B* mixture,

$$Z_{AB} = z_A^{N_A}\,x\,z_B^{N_B} = V_{AB}^{(N_A+N_B)}\left(\frac{2\pi\, m_A\, kT}{h^2}\right)^{\frac{3N_A}{2}}\left(\frac{2\pi\, m_B\, kT}{h^2}\right)^{\frac{3N_B}{2}}$$

Taking logarithms we have

$$\ln Z_{AB} = (N_A + N_B)\ln V_{AB} + \frac{3N_A}{2}\ln\left(\frac{2\pi\, m_A kT}{h^2}\right) + \frac{3N_B}{2}\ln\left(\frac{2\pi\, m_B kT}{h^2}\right)$$

and differentiating with respect to *T* gives

$$\left(\frac{\partial \ln Z_{AB}}{\partial T}\right)_V = \frac{3}{2T}(N_A + N_B)$$

For pure A the corresponding terms are

$$\ln Z_A = N_A \ln V_A + \frac{3N_A}{2} \ln\left(\frac{2\pi m_A kT}{h^2}\right)$$

and

$$\left(\frac{\partial \ln Z_A}{\partial T}\right)_V = \frac{3N_A}{2T}$$

and similarly for component B. When above four equations are combined with Eqs. (7-7) and (2-9) we obtain

$$\frac{\Delta S}{k} = (N_A + N_B) \ln V_{AB} - N_A \ln V_A - N_B \ln V_B$$

For an equimolar mixture we have

$$N_A = N_B = \frac{N_{AB}}{2}$$

from which it follows that

$$V_A = V_B = \frac{V_{AB}}{2}$$

and the entropy of mixing is

$$\Delta S = k(N_A + N_B) \ln 2$$

For a mol of mixture this becomes

$$\Delta s = \frac{\Delta S}{n_A + n_B} = R \ln 2$$

The Corrected Approach

The indistinguishability of particles requires that the naive mixture partition function, Z_{AB}, be divided by the product $N_A!N_B!$ in order to obtain the corrected partition function, Z'_{AB}.

$$Z'_{AB} = \frac{Z_{AB}}{N_A! x N_B!}$$

On taking logarithms we have

$$\ln Z'_{AB} = \ln Z_{AB} - \ln N_A! - \ln N_B!$$

which can be differentiated to obtain

$$\left(\frac{\partial \ln Z'_{AB}}{\partial T}\right)_v = \left(\frac{\partial \ln Z_{AB}}{\partial T}\right)_v$$

For a pure gas it was shown in Sec. 2.3.2 that

$$Z'_A = \frac{Z_A}{N_A!}$$

which leads to

$$\ln Z'_A = \ln Z_A - \ln N_A!$$

and

$$\left(\frac{\partial \ln Z'_A}{\partial T}\right)_v = \left(\frac{\partial \ln Z_A}{\partial T}\right)_v$$

Because the derivatives for the corrected approach are the same as those of the naive approach, there will be no correction to the entropy of mixing arising from the second right-hand term of Eq. (2-9). From the above equations it is easily shown that

$$\ln Z_{A'B} - \ln Z_{A'} - \ln Z_{B'} = \ln Z_{AB} - \ln Z_A - \ln Z_B$$

and there is also no correction arising from the first right-hand term of Eq. (2-9). Therefore, both the naive approach and the corrected approach yield the same entropy of mixing when the gases are different.