

S2.A. Cooling and Liquefaction of Gases

In general, the interaction between two neutral molecules consists of a hard (impenetrable) inner core and a short-range attractive outer region. If a gas of such molecules is allowed to expand, it must do work against the attractive forces so that its temperature will decrease. This rather small effect is called **free expansion cooling**. It can be turned into a cyclic process by throttling the gas repeatedly through a porous plug or constriction. In fact, liquefaction of gases is often done this way in laboratories.

S2.A.1. The Joule Effect: Free Expansion Cooling

In a **Joule effect** experiment, a gas, initially in a small chamber of volume V_i and pressure P_i , is released into a much larger, evacuated, chamber. When the gas finally settles down, its pressure is P_f throughout the combined chamber of volume V_f . The walls of the chambers are immobile and insulated so that the process causes no work, heat, or matter transferred to the environment, i.e.,

$$\Delta Q = 0 \quad \Delta W = 0 \quad \Delta n = 0 \quad (2.188a)$$

The 1st law then gives

$$\Delta U = \Delta Q - \Delta W = 0 \quad (2.188b)$$

Choosing (T, V, n) as the independent variables, we have

$$(dU)_n = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV \quad (2.188)$$

Combining (2.188b) & (2.188) gives

$$\begin{aligned} dT &= -\frac{\left(\frac{\partial U}{\partial V}\right)_{T,n}}{\left(\frac{\partial U}{\partial T}\right)_{V,n}} dV \\ &= \left(\frac{\partial T}{\partial V}\right)_{U,n} dV \quad [(2.6) \text{ used. }] \end{aligned} \quad (2.189)$$

The temperature change due to the expansion is therefore

$$\Delta T = \int_{V_i}^{V_f} \left(\frac{\partial T}{\partial V}\right)_{U,n} dV \quad (2.189a)$$

where $\left(\frac{\partial T}{\partial V}\right)_{U,n}$ is called the **Joule coefficient**.

Using (2.8), we have

$$\begin{aligned} \left(\frac{\partial U}{\partial V}\right)_{T,n} &= \left(\frac{\partial U}{\partial V}\right)_{S,n} + \left(\frac{\partial U}{\partial S}\right)_{V,n} \left(\frac{\partial S}{\partial V}\right)_{T,n} \\ &= -P + T \left(\frac{\partial S}{\partial V}\right)_{T,n} \quad [(2.68-9) \text{ used. }] \\ &= -P + T \left(\frac{\partial P}{\partial T}\right)_{V,n} \quad [(2.100) \text{ used. }] \end{aligned} \quad (2.190)$$

Also, from (2.135), we have

$$\left(\frac{\partial U}{\partial T}\right)_{V,n} = C_{V,n} \quad (2.190a)$$

so that (2.189) gives

$$\left(\frac{\partial T}{\partial V}\right)_{U,n} = -\frac{1}{C_{V,n}} \left[-P + T \left(\frac{\partial P}{\partial T}\right)_{V,n} \right] \quad (2.190b)$$

For an ideal gas,

$$PV = nRT$$

so that

$$\left(\frac{\partial P}{\partial T}\right)_{V,n} = \frac{nR}{V} = \frac{P}{T}$$

and (2.190b) gives

$$\left(\frac{\partial T}{\partial V}\right)_{U,n} = 0 \quad \text{for an ideal gas.} \quad (2.190c)$$

Therefore, there is no temperature change in the free expansion of an ideal gas.

Now, the temperature of a system is just a measure of its average kinetic energy. Since the internal energy of an ideal gas is purely kinetic, its Joule effect, which conserves the internal energy, is therefore null.

For a van der Waals gas [see (2.12) of §2.C.3],

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad [a, b > 0] \quad (2.190d)$$

so that

$$\left(\frac{\partial P}{\partial T}\right)_{V,n} = \frac{nR}{V - nb} = \frac{1}{T} \left(P + \frac{an^2}{V^2}\right) \quad (2.190e)$$

and (2.190b) gives

$$\left(\frac{\partial T}{\partial V}\right)_{U,n} = -\frac{1}{C_{V,n}} \frac{an^2}{V^2} \quad (2.194)$$

< 0 [(2.180) used.]

Hence, there is a temperature drop in the free expansion of a van der Waals gas.

Using (2.146), we have

$$\left(\frac{\partial C_{V,n}}{\partial V}\right)_{T,n} = T \left(\frac{\partial^2 P}{\partial T^2}\right)_{V,n} = 0 \quad [(2.190a) \text{ used. }] \quad (2.192)$$

so that

$$C_{V,n} = C_{V,n}(T, n) \quad (2.193)$$

Putting (2.194) into (2.189a) thus gives

$$\begin{aligned} \Delta T &= -\frac{an^2}{C_{V,n}} \int_{V_i}^{V_f} \frac{1}{V^2} dV \\ &= \frac{an^2}{C_{V,n}} \left(\frac{1}{V_f} - \frac{1}{V_i} \right) \end{aligned} \quad (2.195)$$

$$= -\frac{an^2}{C_{V,n} V_i V_f} \Delta V \quad [\Delta V = V_f - V_i] \quad (2.195a)$$

The fraction temperature change is defined as

$$\frac{\Delta T}{T_i} = \frac{a n^2}{C_{V,n} T_i} \left(\frac{1}{V_f} - \frac{1}{V_i} \right) \quad (2.196)$$

The maximum ΔT is obtained by setting $V_f = \infty$, giving

$$(\Delta T)_{\max} = -\frac{a n^2}{C_{V,n} V_i} \quad (2.195b)$$

Now, according to the equipartition theorem,

$$C_{V,n} \approx \frac{1}{2} f n R$$

where f is the number of quadratic terms in the single-particle Hamiltonian of the system, and

$$R \approx 8.314 \text{ J/mol} \cdot \text{K}$$

From Table 2.1 of Reichl's text, we have, for non-inert gases,

$$a \approx 10^{-1} \text{ Pa} \cdot \text{m}^6 / \text{mol}^2 = 10^{-1} \text{ N} \cdot \text{m}^4 / \text{mol}^2 = 10^{-1} \text{ J} \cdot \text{m}^3 / \text{mol}^2$$

so that (2.195b) becomes

$$(\Delta T)_{\max} = -\frac{2a}{f R V_i} \approx -\frac{10^{-2}}{v_i} \quad v_i = \frac{V_i}{n} = \text{molar volume}$$

At standard conditions ($T = 300 \text{ K}$, $P = 1 \text{ atm}$), we have

$$v \approx 22.4 \text{ l} \approx 10^{-2} \text{ m}^3$$

$$\rightarrow (\Delta T)_{\max} \approx -1 \text{ K}$$

The Joule effect is thus rather weak.

This finite Joule effect can be attributed to the attractive interaction between neutral molecules in a van der Waals gas. As the gas expands, this attraction weakens so that the average potential energy of the gas is raised. Since the total energy is preserved, the average kinetic energy, and hence the temperature, must become lower.

S2.A.2. The Joule-Kelvin Effect: Throttling

Since Lord Kelvin was born William Thomson, the effect is also known as the **Joule-Thomson effect**.

In an idealized Joule-Kelvin effect (or throttling) experiment, an insulated chamber with a fixed porous partition in the center is fitted with a frictionless insulated piston at each end [see Fig.2.13].

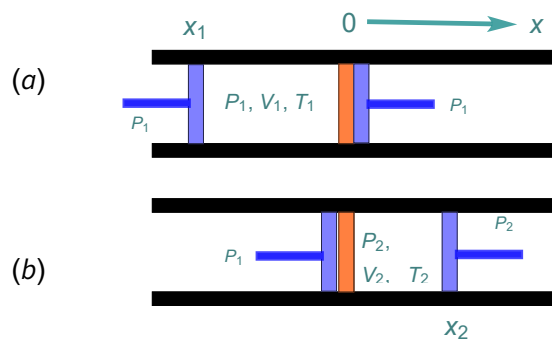


Fig.2.13.

Initially, as shown in Fig.2.13(a), the gas with equilibrium parameters (P_1, V_1, T_1) is entirely on the left hand side of the porous (red) partition. Next, we reduce suddenly the pressure on the right hand side so that $P_2 < P_1$. The gas is thus forced into the right hand side of the porous partition. As it emerges from the holes on the partition, it undergoes sudden expansion and is in a chaotic state due to the turbulence. After equilibrium is reestablished, its parameters become (P_2, V_2, T_2) .

Note that the porous partition divides the gas into separate streams that undergo their own sudden expansion. However, this is not an essential feature of the effect since we can replace the porous partition by one with a single hole. The true difference between the Joule and Joule-Kelvin effects is that ΔT depends on ΔV for the former, but on ΔP for the latter. Furthermore, the latter is readily turned into a cyclic process by alternating the sign of ΔP repeatedly.

Let A be the cross section of the chamber and x_j the position of the piston as measured from the porous partition. The work done by the pistons is

$$\begin{aligned}\Delta W_{\text{pis}} &= \sum_{j=1,2} \mathbf{f}_j \cdot \Delta \mathbf{x}_j \\ &= P_1 A (0 - x_1) - P_2 A (x_2 - 0) \quad [x_1 < 0 \ \& \ x_2 > 0] \\ &= P_1 V_1 - P_2 V_2\end{aligned}$$

The work done by the gas is therefore

$$\begin{aligned}\Delta W &= -\Delta W_{\text{pis}} \\ &= P_2 V_2 - P_1 V_1\end{aligned} \quad (2.197)$$

This round-about way to find ΔW is necessary because P in the recipe $\Delta W = \int P dV$ is not defined for a non-equilibrium process.

Since the system is insulated, $\Delta Q = 0$, and the 1st law gives

$$U_2 - U_1 = \Delta U = -\Delta W = P_1 V_1 - P_2 V_2 \quad [(2.197) \text{ used.}] \quad (2.198)$$

$$\rightarrow H_1 = U_1 + P_1 V_1 = U_2 + P_2 V_2 = H_2 \quad (2.199)$$

$$\therefore \Delta H = H_2 - H_1 = 0 \quad (2.199a)$$

so that the (irreversible) throttling process preserves enthalpy.

From (2.84) of §2.F.2, we have

$$\begin{aligned}(dH)_n &= T dS + V dP \\ &= 0 \quad [(2.199a) \text{ used.}] \end{aligned} \quad (2.200)$$

Choosing (T, P) as independent variables, we have

$$(dS)_n = \left(\frac{\partial S}{\partial T} \right)_{P,n} dT + \left(\frac{\partial S}{\partial P} \right)_{T,n} dP \quad (2.201)$$

so that (2.200) becomes

$$\begin{aligned}(dH)_n &= T \left(\frac{\partial S}{\partial T} \right)_{P,n} dT + \left[T \left(\frac{\partial S}{\partial P} \right)_{T,n} + V \right] dP \\ &= C_{P,n} dT + \left[-T \left(\frac{\partial V}{\partial T} \right)_{P,n} + V \right] dP \quad [(2.144) \ \& \ (2.112) \text{ used.}] \\ &= 0\end{aligned} \quad (2.202)$$

$$= \left(\frac{\partial H}{\partial T} \right)_{P,n} dT + \left(\frac{\partial H}{\partial P} \right)_{T,n} dP \quad [H = H(T, P, n)] \quad (2.202a)$$

$$\rightarrow \frac{dT}{dP} = - \frac{\left(\frac{\partial H}{\partial P} \right)_{T,n}}{\left(\frac{\partial H}{\partial T} \right)_{P,n}} = \frac{1}{C_{P,n}} \left[T \left(\frac{\partial V}{\partial T} \right)_{P,n} - V \right] \quad (2.204a)$$

$$= \left(\frac{\partial T}{\partial P} \right)_{H,n} \quad [(2.5-6) \text{ of } \S 2.B \text{ used. }]$$

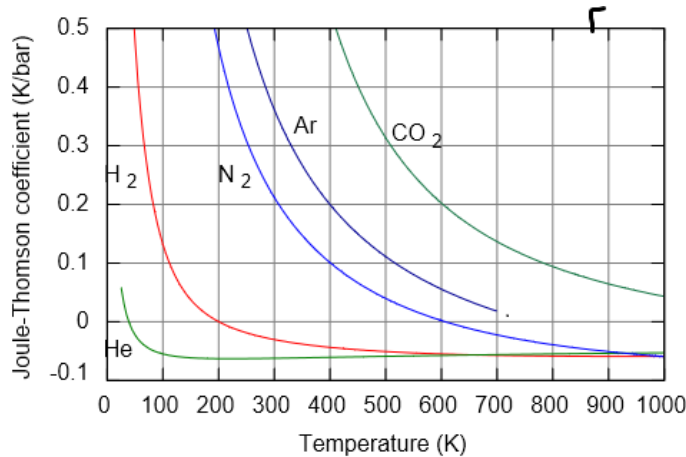
$$\equiv \mu_{JK} = \text{Joule-Kelvin coefficient.} \quad (2.204)$$

$$\therefore \Delta T = \int \mu_{JK} dP \quad (2.204b)$$

Since the gas experiences a pressure drop in the throttling process, we have $dP < 0$ and

$$\begin{aligned} \Delta T < 0 \quad (\text{gas cools}) & \quad \text{if } \mu_{JK} > 0 \\ \Delta T > 0 \quad (\text{gas heats up}) & \quad \text{if } \mu_{JK} < 0 \end{aligned} \quad (2.204c)$$

Temperature dependence of μ_{JK} at $P = 1$ atm is plotted for some common gases in the figure below. Note that H_2 heats up upon expansion for $T \gtrsim 200$ K so that its leakage from storage at room temperature easily causes explosion.



Units of pressure: 1 bar = 10^5 Pa = 0.987 atm.

For an ideal gas, we have

$$PV = nRT$$

$$\rightarrow \left(\frac{\partial V}{\partial T} \right)_{P,n} = \frac{nR}{P} = \frac{V}{T}$$

$$\therefore \mu_{JK} = 0 \quad [(2.204a) \text{ used. }]$$

(2.204b) then gives

$$\Delta T = 0 \quad \text{for an ideal gas.}$$

For a van der Waals gas, $\left(\frac{\partial (2.190 d)}{\partial T} \right)_{P,n}$ gives

$$\left[-\frac{2an^2}{V^3}(V-nb) + \left(P + \frac{an^2}{V^2} \right) \right] \left(\frac{\partial V}{\partial T} \right)_{P,n} = nR$$

$$\rightarrow \left[-\frac{2an^2}{V^3}(V-nb) + \frac{nRT}{V-nb} \right] \left(\frac{\partial V}{\partial T} \right)_{P,n} = nR \quad \text{[(2.190d) used.]}$$

$$\therefore \left(\frac{\partial V}{\partial T} \right)_{P,n} = \frac{nRV^3(V-nb)}{-2an^2(V-nb)^2 + nRTV^3}$$

(2.204a) then gives

$$\begin{aligned} \mu_{JK} &= \frac{1}{C_{P,n}} \left[\frac{nRTV^3(V-nb)}{-2an^2(V-nb)^2 + nRTV^3} - V \right] \\ &= \frac{1}{C_{P,n}} \left[\frac{-n^2RTV^3b + 2an^2(V-nb)^2V}{-2an^2(V-nb)^2 + nRTV^3} \right] \\ &= \frac{1}{nC_{P,n}} \left[\frac{-n^5RTv^3b + 2an^5(v-b)^2v}{-2an^4(v-b)^2 + n^4RTv^3} \right] \quad \left[v = \frac{V}{n}, c_{P,n} = \frac{C_{P,n}}{n} \right] \\ &= \frac{1}{C_{P,n}} \left[\frac{-RTv^3b + 2a(v-b)^2v}{-2a(v-b)^2 + RTv^3} \right] \\ &= \frac{1}{C_{P,n}} \left(\frac{\frac{2a}{RT} \left(\frac{v-b}{v} \right)^2 - b}{1 - \frac{2a}{RTv} \left(\frac{v-b}{v} \right)^2} \right) \end{aligned} \quad (2.205a)$$

Plugging in the ideal gas value $C_{P,n} = \frac{5}{2}nR$, we have

$$\mu_{JK} = \frac{1}{R} \left(\frac{\frac{2a}{RT} \left(\frac{v-b}{v} \right)^2 - b}{\frac{5}{2} - \frac{5a}{RTv} \left(\frac{v-b}{v} \right)^2} \right) \quad (2.205)$$

Consider now the molar van der Waals equation [see (2.190d)]

$$\left(P + \frac{a}{v^2} \right) (v-b) = RT$$

$$\rightarrow P = \frac{RT}{v-b} - \frac{a}{v^2} \quad (2.205b)$$

For low densities, (2.205b) approaches the molar ideal gas law

$$P = \frac{RT}{v}$$

which means

$$v \gg b \quad \& \quad RTv \gg a \quad (2.205c)$$

(2.205) then reduces to

$$\mu_{JK} \approx \frac{2}{5R} \left(\frac{2a}{RT} - b \right) \quad \text{[For low densities.]} \quad (2.206)$$

$$\begin{cases} > 0 & \text{for } T < T_{inv} \\ < 0 & \text{for } T > T_{inv} \end{cases} \quad (2.206a)$$

where

$$T_{\text{inv}} = \frac{2a}{bR} = \text{inversion temperature.} \quad (2.206b)$$

(2.204c) then gives

$$\Delta T < 0 \text{ (gas cools down)} \quad \text{if} \quad T < T_{\text{inv}}$$

$$\Delta T > 0 \text{ (gas heats up)} \quad \text{if} \quad T > T_{\text{inv}} \quad (2.206c)$$

A more general expression for T_{inv} is given by setting $\mu_{JK} = 0$ in (2.204) so that

$$T_{\text{inv}} = \frac{V}{\left(\frac{\partial V}{\partial T}\right)_{P,n}} \quad (2.207)$$

For the van der Waals gas, setting $\mu_{JK} = 0$ in (2.205) gives

$$T_{\text{inv}} = \frac{2a}{Rb} \left(\frac{v-b}{v}\right)^2 \quad (2.208)$$

which reduces to (2.206b) for $v \gg b$, as expected.

Solving for v from (2.208), we have

$$\frac{v-b}{v} = \sqrt{\frac{bRT_{\text{inv}}}{2a}}$$

$$\rightarrow v = \frac{b}{1 - \sqrt{\frac{bRT_{\text{inv}}}{2a}}} \quad v-b = \frac{b \sqrt{\frac{bRT_{\text{inv}}}{2a}}}{1 - \sqrt{\frac{bRT_{\text{inv}}}{2a}}}$$

Putting this into the molar vdW equation (2.205b), we get

$$P = \frac{RT_{\text{inv}}}{b} \left(\sqrt{\frac{2a}{bRT_{\text{inv}}}} - 1 \right) - \frac{a}{b^2} \left(1 - \sqrt{\frac{bRT_{\text{inv}}}{2a}} \right)^2$$

$$= \frac{1}{b} \sqrt{\frac{2aRT_{\text{inv}}}{b}} - \frac{RT_{\text{inv}}}{b} - \frac{a}{b^2} \left(1 - 2\sqrt{\frac{bRT_{\text{inv}}}{2a}} + \frac{bRT_{\text{inv}}}{2a} \right)$$

$$= \frac{2}{b} \sqrt{\frac{2aRT_{\text{inv}}}{b}} - \frac{3RT_{\text{inv}}}{2b} - \frac{a}{b^2} \quad (2.209)$$

$$\rightarrow \frac{dP}{dT_{\text{inv}}} = \frac{1}{b} \sqrt{\frac{2aR}{bT_{\text{inv}}}} - \frac{3R}{2b}$$

$$\frac{d^2P}{dT_{\text{inv}}^2} = -\frac{1}{2b} \sqrt{\frac{2aR}{bT_{\text{inv}}^3}} < 0$$

Therefore, P has at maximum at

$$T_{\text{inv}} = \frac{2aR}{b} \left(\frac{2}{3R} \right)^2 = \frac{8a}{9bR} \quad (2.209a)$$

with value

$$P_{\max} = \frac{2}{b} \sqrt{\frac{2aR}{b} \cdot \frac{8a}{9bR} - \frac{3R}{2b} \cdot \frac{8a}{9bR} - \frac{a}{b^2}} = \frac{a}{3b^2} \quad (2.209b)$$

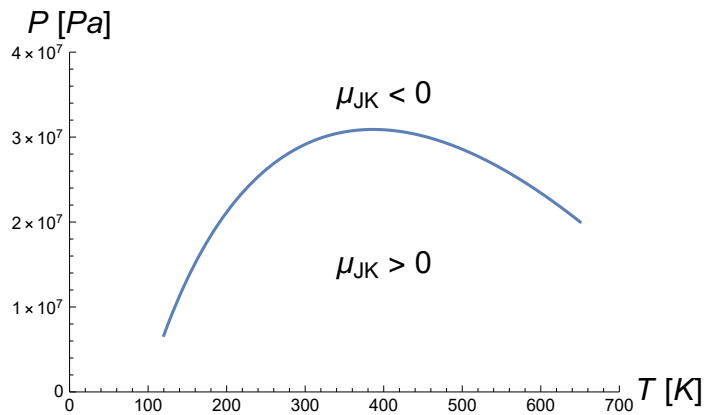
For a N_2 gas, Table 2.1 of §2.C.3 gives [caution: units of b in Reichl's table should be L/mol .]

$$a \approx 0.141 \text{ Pa m}^6/\text{mol} \quad b \approx 0.039 \times 10^{-3} \text{ m}^3/\text{mol}$$

so that

$$P_{\max} \approx 3.07 \times 10^7 \text{ Pa}$$

The plot of (2.209) for a N_2 gas is shown in the figure below [see Reichl's Fig.2.14 for a comparison with experimental data].



If we ignore the small pressure dependence of μ_{JK} , (2.204b) becomes

$$\Delta T \approx \mu_{JK} \Delta P$$

Thus, there is an approximately constant temperature drop under a given pressure drop, if the gas remains in the $\mu_{JK} > 0$ region. The cooling process can therefore be turned into a cycle that forces the gas to go through a pressure drop, and hence a temperature drop, repeatedly. This is called the **Hampson-Linde cycle** and can be used to liquefy atmospheric gases.

Code

```
par = {R → 8.314, a → 0.141, b → 0.039 × 10-3};
P =  $\frac{2}{b} \sqrt{\frac{2aRT}{b} - \frac{3RT}{2b} - \frac{a}{b^2}}$ ;
Plot[P /. par, {T, 120, 650}, PlotRange → {{0, 700}, {0, 4 × 107}},
  AxesLabel → {"T [K]", "P [Pa]"},
  Epilog → {Text["μJK > 0", {400, 1.5 × 107}],
    Text["μJK < 0", {400, 3.5 × 107}]}
```


S2.B. Entropy of Mixing and the Gibbs Paradox

Consider an ideal gas composed of n_j moles of type j molecules, where $j = 1, \dots, m$. The gas is in a container of volume V at temperature T and pressure P . Let

$$n = \sum_{j=1}^m n_j$$

then the equation of state can be written as

$$P = \frac{n R T}{V} = \sum_{j=1}^m n_j \frac{R T}{V} \equiv \sum_{j=1}^m P_j \quad (2.210)$$

where

$$P_j = n_j \frac{R T}{V} \quad (2.211)$$

is called the **partial pressure** of the type j molecules.

The **mole fraction** is defined as

$$x_j \equiv \frac{n_j}{n} = \frac{n_j}{\sum_{k=1}^m n_k} \quad (2.212a)$$

$$= \frac{P_j}{P} \quad [(2.210-1) \text{ used. }] \quad (2.212)$$

Using

$$\mu_j' dN_j = \mu_j d n_j$$

the definition (2.108) becomes

$$dG = -S dT + V dP + \sum_{j=1}^m \mu_j d n_j \quad (2.213)$$

where μ_j is the (molar) **chemical potential** for type j molecules.

If there is only 1 species of molecules, i.e., $m = 1$, putting (2) of Ex.2.3 in §2.E into (2.107) of §2.F.4 gives

$$\begin{aligned} G &= \mu^{(0)} n \\ &= -n R T \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + G_0 \\ &= -n R T \ln \left(\frac{T^{5/2}}{P} \right) + G^{(0)} \end{aligned} \quad (2.214)$$

where $\mu^{(0)}$ is the species-independent chemical potential of an ideal gas and

$$G_0 = G(T_0, P_0, n) \quad G^{(0)} = G_0 + n R T_0 \ln \frac{T_0^{5/2}}{P_0} \quad (2.214a)$$

Next, we consider the “unmixed” version of the gas. Thus, the container is divided into m compartments, each holding a single species of gas. The walls of the compartments are mobile and heat conducting so that, in equilibrium, every compartment have the same T and P . The Gibbs free energy is then simply

$$G_{\text{um}} = - \sum_{j=1}^m n_j \mu^{(0)}$$

$$= -\sum_{j=1}^m n_j R T \ln \left(\frac{T^{5/2}}{P} \right) + G_{\text{um}}^{(0)} \quad (2.215)$$

By removing the walls, we obtain the “mixed” version of the gas. Since there is no interaction between the molecules, each type of gas occupy the container as if the other type of gases do not exist. Hence,

$$\begin{aligned} G_{\text{mix}} &= -\sum_{j=1}^m n_j \mu^{(0)}(T, P_j) \\ &= -\sum_{j=1}^m n_j R T \ln \left(\frac{T^{5/2}}{P_j} \right) + G_{\text{mix}}^{(0)} \end{aligned} \quad (2.215a)$$

$$\begin{aligned} &= -\sum_{j=1}^m n_j R T \ln \left(\frac{T^{5/2}}{P x_j} \right) + G_{\text{mix}}^{(0)} \quad [(2.212) \text{ used. }] \\ &= G_{\text{um}} - G_{\text{um}}^{(0)} + \sum_{j=1}^m n_j R T \ln x_j + G_{\text{mix}}^{(0)} \quad [(2.215) \text{ used. }] \end{aligned} \quad (2.216)$$

Thus, the change in the Gibbs energy upon mixing is

$$\begin{aligned} \Delta G &\equiv G_{\text{mix}} - G_{\text{um}} \\ &= \sum_{j=1}^m n_j R T \ln x_j + G_{\text{mix}}^{(0)} - G_{\text{um}}^{(0)} \end{aligned} \quad (2.217)$$

From (2.109) of §2.F.4, we obtain the corresponding change in entropy as

$$\begin{aligned} \Delta S &= -\left(\frac{\partial \Delta G}{\partial T} \right)_{P, \{n_j\}} \\ &= -\sum_{j=1}^m n_j R \ln x_j \end{aligned} \quad (2.218)$$

$$\geq 0 \quad [0 < x_j \leq 1] \quad (2.218a)$$

where the equal sign holds only for $m = 1$ so that $x_1 = 1$.

Hence, entropy always increases after mixing.

Since (2.218) is independent of the species of molecules in the gas, it should hold when the gases in the m compartments are all of the same type, i.e., when a gas mixes with itself. In which case, the result $\Delta S > 0$ given by (2.218) is contrary to the self-evident value of $\Delta S = 0$. This is called the **Gibbs paradox** and can be resolved only by introducing the (quantum mechanical) concept of identical (or indistinguishable) particles.

S2.C. Osmotic Pressure in Dilute Solutions

Osmosis is demonstrated by the setup shown in Fig.2.16.

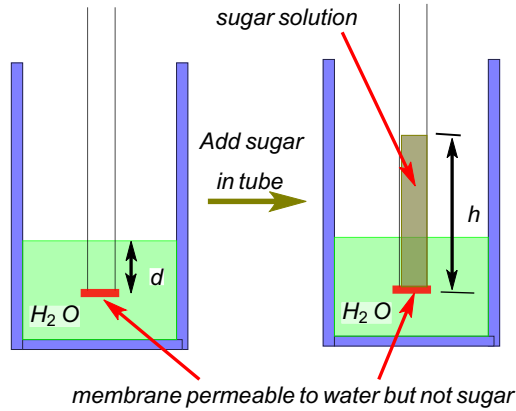


Fig.2.16.

To begin, a tube with one end closed with a membrane permeable only to water is immersed into a beaker of water. The water levels in and outside the tube are equal. If sugar is added inside the tube, level of the sugar solution will rise. The phenomenon is called **osmosis**.

With reference to Fig.2.16, the pressures at the membrane after equilibrium is established are

$$P_{\text{inside}} = P_{\text{atm}} + \rho_s h g = P_{\text{outside}} = P_{\text{atm}} + \rho_w d g \quad (2.219a)$$

where

P_{atm} = atmospheric pressure

ρ_s = density of sugar solution

ρ_w = density of water

g = acceleration of gravity

h = height of sugar solution

d = depth of membrane

The **osmotic pressure** is the excess pressure caused by the sugar solute,

$$\begin{aligned} \pi &= P_{\text{inside}} - P_{\text{outside}} \\ &= (\rho_s h - \rho_w d) g \\ &\approx \rho_s (h - d) g \quad \text{for dilute solution } (\rho_s \approx \rho_w) \end{aligned} \quad (2.219b)$$

An equivalent setup of the phenomenon is shown in Fig.2.17, where the role of π is depicted more clearly.

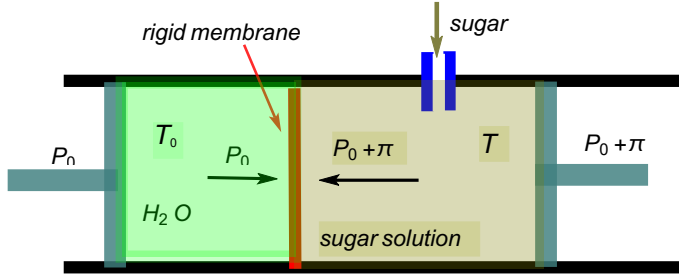


Fig.2.17.

The Gibbs free energy for pure water is defined as

$$dG_{H_2O} = -SdT + VdP + \mu_w^{(0)} dn_w \quad (2.219b)$$

For the sugar solution,

$$dG_{sol} = -SdT + VdP + \mu_w dn_w + \mu_s dn_s \quad (2.219)$$

where the subscripts *w* & *s* denote the water and sugar components, respectively.

From the Gibbs-Duhem equation [see (2.62) of §2.E], we see that the chemical potentials are intensive variables that depend only on *T*, *P*, & the **molar fractions** [see (2.65)].

$$x_j = \frac{n_j}{n} \quad n = \sum_k n_k \quad (2.220a)$$

$$\rightarrow \sum_j x_j = 1 \quad (2.220b)$$

Owing to (2.220b), only one molar fraction is independent in a two-component system.

Consider now the setup in Fig.2.17. Since the membrane is rigid and impermeable to sugar, the conditions for thermodynamic equilibrium are

$$T = T_0 \quad \text{and} \quad \mu_w^{(0)}(T_0, P_0) = \mu_w(T, P_0 + \pi, x_s) \quad (2.221)$$

where we have chosen *x_s* as the independent molar fraction.

Using the results of Ex.2.9 in §2.H.2, we set

$$G_{sol} = n_w \mu_w^{(0)}(T, P) + n_s \mu_s^{(0)}(T, P) + RT n_w \ln x_w + RT n_s \ln x_s + \lambda \frac{n_w n_s}{n} \quad (2.222)$$

where $\mu_s^{(0)}$ is the chemical potential for pure sugar. We shall assume $\lambda < 0$ (i.e., attractive interactions)

so that the condition $T > \frac{\lambda}{2R}$ for a single phase (i.e., no sugar precipitation) is satisfied for all *T* [see

Figure in Ex.2.9].

Note: By definition, μ_j is the increase of the system energy if we add 1 mole of the type *j* molecules into the system. If $\lambda < 0$, then (2.222) shows that this energy change is reduced if $n_k \neq 0$ for $k \neq j$. Therefore, the interaction between types *j* & *k* molecules must be attractive.

Using (2.111) of §2.F.4 and

$$\frac{\partial x_k}{\partial n_j} = \frac{\partial}{\partial n_j} \left(\frac{n_k}{n} \right) = \frac{\delta_{jk}}{n} - \frac{n_k}{n^2} = \frac{\delta_{jk} - x_k}{n}$$

we have

$$\mu_w(T, P, x_s) = \left(\frac{\partial G_{sol}}{\partial n_w} \right)_{T, P, n_s}$$

$$\begin{aligned}
&= \mu_W^{(0)}(T, P) + RT \left[\ln x_W + \frac{n_W}{x_W} \left(\frac{1 - x_W}{n} \right) \right] + RT \frac{n_s}{x_s} \left(-\frac{x_s}{n} \right) + \lambda \left(\frac{n_s}{n} - \frac{n_W n_s}{n^2} \right) \\
&= \mu_W^{(0)}(T, P) + RT \ln x_W + \lambda (x_s - x_W x_s) \\
&= \mu_W^{(0)}(T, P) + RT \ln (1 - x_s) + \lambda x_s^2 \tag{2.223} \\
&= \mu_W^{(0)}(T, P) - x_s RT + O(x_s^2) \quad \text{[For dilute solution.]} \tag{2.224}
\end{aligned}$$

Using the Maxwell relation (2.114) of §2.F.4, we have, for pure water,

$$\begin{aligned}
\left(\frac{\partial \mu_W^{(0)}}{\partial P} \right)_{T, n_w} &= \left(\frac{\partial V}{\partial n_W} \right)_{T, P} \\
&= v_W^{(0)} = \text{molar volume of pure water.}
\end{aligned}$$

$$\rightarrow \mu_W^{(0)}(T, P) = \int dP v_W^{(0)} + c(T) \quad [c(T) = \text{arbitrary function of } T.]$$

Since water is highly incompressible, $v_W^{(0)}$ is nearly independent of P . Hence,

$$\begin{aligned}
\mu_W^{(0)}(T, P) &\approx \mu_W^{(0)}(T, P_0) + v_W^{(0)}(P - P_0) \\
&= \mu_W^{(0)}(T, P_0) + v_W^{(0)} \pi \tag{2.225}
\end{aligned}$$

so that (2.224) becomes

$$\mu_W(T, P, x_s) \approx \mu_W^{(0)}(T, P_0) + v_W^{(0)} \pi - x_s RT$$

Putting in the equilibrium condition (2.221), we have

$$\begin{aligned}
\pi &= \frac{x_s}{v_W^{(0)}} RT \\
&= \frac{n_s}{V^{(0)}} RT \tag{2.225a}
\end{aligned}$$

where

$$V^{(0)} = n v_W^{(0)}$$

For a dilute solution,

$$V = n_W v_W^{(0)} + n_s v_s^{(0)} \approx n v_W^{(0)}$$

so that (2.225a) becomes

$$\pi \approx \frac{n_s}{V} RT \tag{2.226}$$

which is known as the **van't Hoff's law**. Thus, the solute acts like an ideal gas inside the solution with a partial pressure π . This is to be expected since the interactions between the solute and the solvent can be ignored for dilute solutions [see (2.223-4)].

Ex.2.10.

The osmotic pressure π of a solution containing n_{suc} moles of **sucrose** ($C_{12}H_{22}O_{11}$) and 1 kg of water (H_2O) is measured at $T = 303 \text{ K}$ (30°C). The following result was obtained:

n_{suc} [mole]	π_{exp} [10^5 Pa]
0.1	2.53
0.2	5.17
0.3	7.81

(1)

Compute π using van't Hoff's law and compare the result with experiment.

Answer

The molecular weight of water (H_2O) is

$$M_w = (2 \times 1 + 16) \text{ g/mol} = 18 \text{ g/mol}$$

Therefore, 1 kg of water contains

$$n_w = \frac{1000}{18} \text{ mols} \approx 55.6 \text{ mols}$$

Since the density of water is

$$\rho_w \approx 1 \text{ g/cm}^3 = 10^6 \text{ g/m}^3$$

so that its molar volume is

$$v_w = \frac{M_w}{\rho_w} \approx 18 \times 10^{-6} \text{ m}^3/\text{mol}$$

The van't Hoff's law (2.226) then becomes

$$\begin{aligned} \pi &= \frac{n_{\text{suc}}}{n_w v_w} R T && (T = 303 \text{ K}, R \approx 8.31 \text{ J/K} \cdot \text{mol}) \\ &\approx \frac{n_{\text{suc}}}{55.6 \times 18 \times 10^{-6}} \times 8.31 \times 303 \\ &\approx 2.52 \times 10^6 n_{\text{suc}} \text{ [Pa]} \end{aligned} \quad (2)$$

which gives

n_{suc} [mole]	π_{vH} [10^5 Pa]	$\frac{\pi_{\text{vH}} - \pi_{\text{exp}}}{\pi_{\text{vH}}} \times 100\%$
0.1	2.52	-0.56%
0.2	5.03	-2.7%
0.3	7.55	-3.5%

Excellent agreements are found.

Code

$$a = \frac{8.31 \times 303}{55.6 \times 18 \times 10^{-6}}$$

$$\pi_{\text{vH}} = \{.1, .2, .3\} a$$

$$\pi_{\text{exp}} = \{2.53, 5.17, 7.81\} 10^5$$

$$2.51592 \times 10^6$$

$$\{251592., 503183., 754775.\}$$

$$\{253000., 517000., 781000.\}$$

$$\pi_{\text{vH}} - \pi_{\text{exp}}$$

$$\{-1408.27, -13816.5, -26224.8\}$$

$$\frac{\pi_{\text{vH}} - \pi_{\text{exp}}}{\pi_{\text{vH}}} 100$$

$$\{-0.559746, -2.74583, -3.47452\}$$

Read Reichl's introductory remarks for §S2.D.

S2.D.1. The Affinity

Consider the chemical reaction



where the **stoichiometric coefficient** $|v_j|$ indicates the number of type j molecules required for a single reaction. For some reason to be made clear later [see (2.235)], we have used the convention

$$v_A, v_B \leq 0 \quad v_C, v_D \geq 0 \quad (2.227a)$$

Consider now the forward (left to right) reaction. Its occurrence implies a number $|v_A|$ of A molecules have collided with a number $|v_B|$ of B molecules and reacted. Let N_j be the number of type j molecules present. The probability of finding a type j molecule is therefore

$$p_j = \frac{N_j}{N} \quad N = \sum_j N_j$$

Since $N_j \gg |v_j|$, the probability of finding a cluster of molecules consisting of $|v_A|$ type A and $|v_B|$ type B molecules is approximately

$$C_{|v_A|+|v_B|}^{|v_A|+|v_B|} \left(\frac{N_A}{N}\right)^{|v_A|} \left(\frac{N_B}{N}\right)^{|v_B|}$$

where $C_k^n = \frac{n!}{(n-k)!k!}$ is the k -combination of n things.

Let r_1 be the **rate of the forward reaction** (number of forward reactions per unit time). By lumping all the kinetic effects of the reactions into a **rate constant** k_1 , we can write

$$r_1 = k_1 N_A^{|v_A|} N_B^{|v_B|} \quad (2.228a)$$

Similarly, for the backward (right to left) reaction,

$$r_2 = k_2 N_C^{|v_C|} N_D^{|v_D|} \quad (2.228b)$$

Now, in each forward reaction,

$$\begin{aligned} \Delta N_A &= -|v_A| = v_A & \Delta N_B &= -|v_B| = v_B \\ \Delta N_C &= |v_C| = v_C & \Delta N_D &= |v_D| = v_D \end{aligned}$$

while for each backward reaction,

$$\begin{aligned} \Delta N_A &= |v_A| = -v_A & \Delta N_B &= |v_B| = -v_B \\ \Delta N_C &= -|v_C| = -v_C & \Delta N_D &= -|v_D| = -v_D \end{aligned}$$

Therefore, the net reaction rate is

$$\begin{aligned} r_1 - r_2 &= k_1 N_A^{|v_A|} N_B^{|v_B|} - k_2 N_C^{|v_C|} N_D^{|v_D|} \\ &= -\frac{1}{|v_A|} \frac{dN_A}{dt} = -\frac{1}{|v_B|} \frac{dN_B}{dt} = \frac{1}{|v_C|} \frac{dN_C}{dt} = \frac{1}{|v_D|} \frac{dN_D}{dt} \end{aligned} \quad (2.228)$$

Dividing (2.228) by the Avogadro number \mathcal{N}_a , we get

$$\frac{dn_A}{v_A} = \frac{dn_B}{v_B} = \frac{dn_C}{v_C} = \frac{dn_D}{v_D} \equiv d\xi = \left(\frac{r_1 - r_2}{\mathcal{N}_a}\right) dt \quad (2.235)$$

where ξ is called the **degree of reaction**. Thus,

$$\begin{aligned} d\xi > 0 & \quad \text{if forward reaction prevails} \quad (r_1 > r_2) \\ d\xi < 0 & \quad \text{if backward reaction prevails} \quad (r_2 > r_1) \end{aligned} \quad (2.235a)$$

Consider now the case where there are excess type B & D molecules so that initially,

$$\begin{aligned} n_A &= |v_A| n_0 & n_B &= |v_B| n_0 + \tilde{n}_B \\ n_C &= |v_C| n_0' & n_D &= |v_D| n_0' + \tilde{n}_D \end{aligned} \quad (2.229a)$$

If the conditions are favorable to the forward reaction, then the system will reach equilibrium when all type A molecules are exhausted, leaving

$$\begin{aligned} n_A &= 0 & n_B &= \tilde{n}_B \\ n_C &= v_C(n_0 + n_0') & n_D &= v_D(n_0 + n_0') + \tilde{n}_D \end{aligned} \quad (2.229b)$$

In general, after $m \mathcal{N}_a$ forward reactions, we have

$$\begin{aligned} n_A &= -v_A n_0 + m v_A & n_B &= -v_B n_0 + \tilde{n}_B + m v_B \\ n_C &= v_C n_0' + m v_C & n_D &= v_D n_0' + \tilde{n}_D + m v_D \end{aligned} \quad (2.229c)$$

Comparing (2.229c) with (2.235) gives

$$\begin{aligned} dm &= d\xi \\ \rightarrow m &= \xi + c \quad [c = \text{const}] \end{aligned} \quad (2.229d)$$

(2.229c) thus becomes

$$\begin{aligned} n_A &= -v_A(n_0 - c) + \xi v_A & n_B &= -v_B(n_0 - c) + \tilde{n}_B + \xi v_B \\ n_C &= v_C(n_0' + c) + \xi v_C & n_D &= v_D(n_0' + c) + \tilde{n}_D + \xi v_D \end{aligned}$$

Setting $c = -n_0'$ then gives

$$\begin{aligned} n_A &= -v_A(n_0 + n_0') + \xi v_A & n_B &= -v_B(n_0 + n_0') + \tilde{n}_B + \xi v_B \\ n_C &= \xi v_C & n_D &= \tilde{n}_D + \xi v_D \end{aligned} \quad (2.230-3)$$

Solving (2.230) gives

$$\xi = \frac{n_A}{v_A} + (n_0 + n_0') \quad (2.229)$$

so that (2.229d) becomes

$$\begin{aligned} m &= \frac{n_A}{v_A} + n_0 & (2.229e) \\ &= \frac{n_A - n_{A0}}{v_A} \end{aligned}$$

where n_{A0} is the initial value of n_A [see (2.229b)].

Note that, like energies, only the difference $d\xi$ is physically significant.

Chemical reactions experiments are often carried out under constant T & P , which makes the Gibbs free energy G the natural choice of thermodynamic potential. Putting (2.235) into (2.108) of §2.F.4 gives

$$\begin{aligned} dG &= -SdT + VdP + \sum_{j=1}^m \mu_j n_j \\ &= -SdT + VdP + \mathcal{A}d\xi \end{aligned} \quad (2.236)$$

where

$$\mathcal{A} = \sum_{j=1}^m \mu_j \nu_j \quad (2.238)$$

is called the **affinity**. Hence,

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = \mathcal{A} = \sum_{j=1}^m \mu_j \nu_j \quad (2.237)$$

At chemical equilibrium, G is at a minimum so that

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P}^0 = \mathcal{A}^0 = 0 \quad (2.239)$$

By the same token, spontaneous approach towards equilibrium must satisfy

$$\begin{aligned} (dG)_{T,P} &= \left(\frac{\partial G}{\partial \xi} \right)_{T,P} d\xi = \mathcal{A} d\xi \\ &< 0 \end{aligned} \quad (2.240)$$

For the reaction (2.227), this means [see (2.235a)]

1. If the forward reaction prevails, i.e., $d\xi > 0$, then $\mathcal{A} < 0$.
2. If the backward reaction prevails, i.e., $d\xi < 0$, then $\mathcal{A} > 0$.

Generalization to the case where there are r chemical reactions in the system is straightforward. To begin, (2.235) becomes, for the k^{th} reaction

$$\frac{dn_j}{\nu_{jk}} = d\xi_k \quad j = 1, \dots, m \ \& \ k = 1, \dots, r$$

so that for the whole system

$$dn_j = \sum_{k=1}^r \nu_{jk} d\xi_k \quad (2.241)$$

We can derive some useful results by treating the reactants as ideal gases. To begin, using (2) of Ex.2.3 in §2.E gives

$$\mu_j(T, P_j) = -RT \ln \left[\frac{P_0}{P_j} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \quad (2.242)$$

where P_j is the partial pressure for type j molecules [see §S.2B] and

$$\mu_j^0 = \mu_j(T_0, P_0)$$

Hence,

$$\begin{aligned} G(T, P, \xi) &= \sum_{j=1}^m n_j \mu_j \\ &= \sum_{j=1}^m n_j \left\{ -RT \ln \left[\frac{P_0}{P_j} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \right\} \\ &= \sum_{j=1}^m n_j \left\{ -RT \ln \left[\frac{P_0}{P x_j} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \right\} \quad [(2.212) \ \S 2.B \text{ of used. }] \\ &= \sum_{j=1}^m n_j \left\{ -RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \right\} + RT \sum_{j=1}^m n_j \ln x_j \\ &= \sum_{j=1}^m n_j \left\{ -RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \right\} + RT \ln \left(\prod_{j=1}^m x_j^{n_j} \right) \end{aligned} \quad (2.243a)$$

For the reaction (2.227),

$$G(T, P, \xi) = \sum_{j=A,B,C,D} n_j \left\{ -RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \right\} + RT \ln (x_A^{n_A} x_B^{n_B} x_C^{n_C} x_D^{n_D}) \quad (2.243)$$

Similarly, (2.238) becomes

$$\begin{aligned} \mathcal{A}(T, P, \xi) &= \sum_{j=1}^m \nu_j \left\{ -RT \ln \left[\frac{P_0}{P_j} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \right\} \\ &= \sum_{j=1}^m \nu_j \left\{ -RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \right\} + RT \ln \left(\prod_{j=1}^m x_j^{\nu_j} \right) \end{aligned} \quad (2.244a)$$

For the reaction (2.227),

$$\mathcal{A}(T, P, \xi) = \sum_{j=A,B,C,D} \nu_j \left\{ -RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + \mu_j^0 \right\} + RT \ln \left(\frac{x_C^{\nu_C} x_D^{\nu_D}}{x_A^{|\nu_A|} x_B^{|\nu_B|}} \right) \quad (2.244)$$

At equilibrium, $\mathcal{A} = 0$, and we have

$$\ln \left(\frac{x_C^{\nu_C} x_D^{\nu_D}}{x_A^{|\nu_A|} x_B^{|\nu_B|}} \right) = \sum_{j=A,B,C,D} \nu_j \left\{ \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] - \frac{\mu_j^0}{RT} \right\} \quad (2.245)$$

which is known as the **law of mass action**. See Ex 2.11 for its application.

S2.D.2. Stability

In contrast to the stability analysis in §2.H that based on S being a maximal at equilibrium, the discussion here is based on G being a minimum there. With G given by (2.236) of §S2.D.1, this means

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P}^0 = \mathcal{A}^0 = 0 \quad (2.246)$$

and

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,P}^0 = \left(\frac{\partial \mathcal{A}}{\partial \xi}\right)_{T,P}^0 > 0 \quad (2.247)$$

Putting

$$H = G + TS$$

into (2.246) gives

$$\begin{aligned} \left(\frac{\partial H}{\partial \xi}\right)_{T,P}^0 &= T \left(\frac{\partial S}{\partial \xi}\right)_{T,P}^0 \\ &= \text{heat of reaction} \\ &= \text{heat absorbed by each reaction} \end{aligned} \quad (2.248)$$

Thus,

$$\begin{aligned} \left(\frac{\partial H}{\partial \xi}\right)_{T,P}^0 > 0 & \quad \text{for endothermic (heat absorbing) reactions.} \\ \left(\frac{\partial H}{\partial \xi}\right)_{T,P}^0 < 0 & \quad \text{for exothermic (heat releasing) reactions.} \end{aligned} \quad (2.248a)$$

Obviously, if the forward reaction is endothermic, the backward reaction must be exothermic, and vice versa.

Using,

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,\xi} \quad [\text{See (2.236).}]$$

(2.248) can be written as

$$\begin{aligned} \left(\frac{\partial H}{\partial \xi}\right)_{T,P}^0 &= -T \left[\frac{\partial}{\partial \xi} \left(\frac{\partial G}{\partial T} \right)_{P,\xi} \right]_{T,P}^0 \\ &= -T \left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial \xi} \right)_{P,T} \right]_{\xi,P}^0 \\ &= -T \left(\frac{\partial \mathcal{A}}{\partial T} \right)_{\xi,P}^0 \quad [\text{See (2.236).}] \end{aligned} \quad (2.249)$$

Using the ideal gas result [see (2.244) of S2.D.1], this becomes

$$\begin{aligned} \left(\frac{\partial H}{\partial \xi}\right)_{T,P}^0 &= -T \left\{ \sum_{j=A,B,C,D} \nu_j \left\{ -R \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] - \frac{5}{2} R \right\} + R \ln \left(\frac{x_C^{\nu_C} x_D^{\nu_D}}{x_A^{|\nu_A|} x_B^{|\nu_B|}} \right) \right\} \\ &= \nu_t R T \left\{ \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + \frac{5}{2} \right\} - R T \ln \left(\frac{x_C^{\nu_C} x_D^{\nu_D}}{x_A^{|\nu_A|} x_B^{|\nu_B|}} \right) \end{aligned} \quad (2.250)$$

where

$$v_t = \sum_{j=A,B,C,D} v_j \quad (2.250a)$$

= increase (decrease) of the total number of molecules in a forward (backward) reaction.

Using (2) of Ex.2.3 in §2.E, we can write (2.250) as

$$\left(\frac{\partial H}{\partial \xi}\right)_{T,P}^0 = v_t \left[-(\mu - \mu_0) + \frac{5}{2} R T \right] + T \Delta S_{\text{mix}} \quad (2.250b)$$

where [see (2.218) of §2.B]

$$\Delta S_{\text{mix}} = R \ln (x_A^{v_A} x_B^{v_B} x_C^{v_C} x_D^{v_D}) \quad (2.250c)$$

is the increase of entropy due to mixing in each forward reaction.

Note that if the total number of molecules is unchanged, i.e., $v_t = 0$, only the entropy mixing term contributes to the heat of reaction.

Using (2.6) of §2.B, we have, for P fixed,

$$\begin{aligned} \left(\frac{\partial \xi}{\partial T}\right)_{P,\mathcal{A}} &= - \frac{\left(\frac{\partial \mathcal{A}}{\partial T}\right)_{P,\xi}}{\left(\frac{\partial \mathcal{A}}{\partial \xi}\right)_{P,T}} \\ &= \frac{\frac{1}{T} \left(\frac{\partial H}{\partial \xi}\right)_{P,T}}{\left(\frac{\partial \mathcal{A}}{\partial \xi}\right)_{P,T}} \quad [(2.249) \text{ used. }] \end{aligned} \quad (2.251)$$

Setting

$$c = \frac{1}{T \left(\frac{\partial \mathcal{A}}{\partial \xi}\right)_{P,T}^0} > 0 \quad [\text{ See (2.247) }]$$

we have,

$$\Delta \xi \approx c \left(\frac{\partial H}{\partial \xi}\right)_{P,T}^0 \Delta T \quad \text{at equilibrium} \quad (2.251a)$$

Therefore, a small increase in T at equilibrium ($\mathcal{A} = 0$ and no net reactions) will cause ξ to increase for endothermic reactions [$\left(\frac{\partial H}{\partial \xi}\right)_{P,T}^0 > 0$], thus pushing the system off the equilibrium and into the direction of endothermic reactions. This is to be expected since adding heat to the system obviously enables the heat absorbing reactions.

(2.236) implies the Maxwell relation at fixed T ,

$$\left(\frac{\partial \mathcal{A}}{\partial P}\right)_{T,\xi} = \left(\frac{\partial V}{\partial \xi}\right)_{T,P} \quad (2.252)$$

Taking $T \leftrightarrow P$ in (2.251) gives

$$\left(\frac{\partial \xi}{\partial P}\right)_{T,\mathcal{A}} = - \frac{\left(\frac{\partial \mathcal{A}}{\partial P}\right)_{T,\xi}}{\left(\frac{\partial \mathcal{A}}{\partial \xi}\right)_{P,T}}$$

$$= -\frac{\left(\frac{\partial V}{\partial \xi}\right)_{T,P}}{\left(\frac{\partial \mathcal{A}}{\partial \xi}\right)_{P,T}} \quad [(2.252) \text{ used. }] \quad (2.253)$$

Setting

$$c' = \frac{1}{\left(\frac{\partial \mathcal{A}}{\partial \xi}\right)_{P,T}^0} > 0 \quad [\text{ See (2.247) }]$$

we have,

$$\Delta \xi \approx -c' \left(\frac{\partial V}{\partial \xi}\right)_{T,P}^0 \Delta P \quad \text{at equilibrium} \quad (2.251a)$$

Therefore, a small increase in P at equilibrium will cause ξ to increase for reactions that decrease the volume [$\left(\frac{\partial V}{\partial \xi}\right)_{T,P}^0 < 0$], thus pushing the system off the equilibrium and into the direction of the volume decreasing reactions.

Ex. 2.11.

Consider the gaseous reaction



Start with 1 mol of $N_2 O_4$ and no $N O_2$ at temperature T and pressure P . Use the ideal gas values for the chemical potentials.

- Compute and plot $G(T, P, \xi)$ as a function of ξ for
 - $P = 1 \text{ atm}$ and $T = 298 \text{ K}$ (25°C)
 - $P = 1 \text{ atm}$ and $T = 596 \text{ K}$ (323°C)
- Compute and plot $\mathcal{A}(T, P, \xi)$ as a function of ξ for
 - $P = 1 \text{ atm}$ and $T = 298 \text{ K}$ (25°C)
 - $P = 1 \text{ atm}$ and $T = 596 \text{ K}$ (323°C)
- What is ξ at $P = 1 \text{ atm}$ and $T = 298 \text{ K}$?
How many moles of $N_2 O_4$ and $N O_2$ are present at equilibrium?
- If the volume is initially at V_0 , what is the volume at $P = 1 \text{ atm}$ and $T = 298 \text{ K}$?
- What is the heat of reaction $P = 1 \text{ atm}$ and $T = 298 \text{ K}$?

Answer

Using (2.235) on (1a), we have

$$\frac{dn_{N_2 O_4}}{-1} = \frac{dn_{N O_2}}{2} = d\xi$$

$$\rightarrow n_{N_2 O_4} = -\xi + c_1$$

$$n_{N O_2} = 2\xi + c_2 \quad (1b)$$

where c_1 & c_2 are constants. Note that $[\xi] = \text{mole}$.

Initially, we have

$$1 = -\xi(0) + c_1$$

$$0 = 2\xi(0) + c_2$$

where $\xi(0)$ is the value of ξ at time $t = 0$. (1b) thus becomes

$$n_{N_2O_4} = -\xi + 1 + \xi(0) = 1 - \xi'$$

$$n_{NO_2} = 2\xi - 2\xi(0) = 2\xi' \quad (1c)$$

where

$$\xi' = \xi - \xi(0) \quad (1d)$$

Thus,

$$n = n_{N_2O_4} + n_{NO_2} = 1 + \xi' \quad (1e)$$

As mentioned before, only the difference $d\xi$ is physically significant. Therefore, without loss of generality, we can set $\xi(0) = 0$ so that $\xi' = \xi$.

The mole fractions are therefore

$$x_{N_2O_4} = \frac{n_{N_2O_4}}{n} = \frac{1 - \xi}{1 + \xi} \quad x_{NO_2} = \frac{n_{NO_2}}{n} = \frac{2\xi}{1 + \xi} \quad (1)$$

Answer (a)

Putting (1) & (1.c-e) into (2.243a) gives

$$\begin{aligned} G(T, P, \xi) &= -nRT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + n_{N_2O_4} \mu_{N_2O_4}^0 + n_{NO_2} \mu_{NO_2}^0 + RT \ln (x_{N_2O_4}^{n_{N_2O_4}} x_{NO_2}^{n_{NO_2}}) \\ &= -(1 + \xi) RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + (1 - \xi) \mu_{N_2O_4}^0 + 2\xi \mu_{NO_2}^0 + RT \ln \left[\left(\frac{1 - \xi}{1 + \xi} \right)^{1 - \xi} \left(\frac{2\xi}{1 + \xi} \right)^{2\xi} \right] \quad [(1c) \text{ used.}] \\ &= -(1 + \xi) RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + (1 - \xi) \mu_{N_2O_4}^0 + 2\xi \mu_{NO_2}^0 + RT \ln \left[\frac{(1 - \xi)^{1 - \xi}}{(1 + \xi)^{1 + \xi}} (2\xi)^{2\xi} \right] \quad (2) \end{aligned}$$

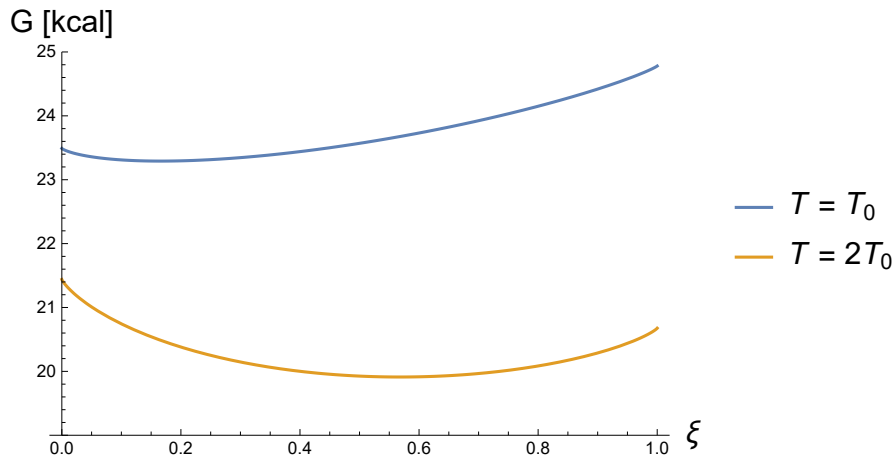
$$\rightarrow G(T_0, P_0, \xi) = (1 - \xi) \mu_{N_2O_4}^0 + 2\xi \mu_{NO_2}^0 + RT_0 \ln \left[\frac{(1 - \xi)^{1 - \xi}}{(1 + \xi)^{1 + \xi}} (2\xi)^{2\xi} \right] \quad (2a)$$

$$\begin{aligned} G(2T_0, P_0, \xi) &= -5(1 + \xi) RT_0 \ln 2 + (1 - \xi) \mu_{N_2O_4}^0 + 2\xi \mu_{NO_2}^0 \\ &\quad + 2RT_0 \ln \left[\frac{(1 - \xi)^{1 - \xi}}{(1 + \xi)^{1 + \xi}} (2\xi)^{2\xi} \right] \quad (2b) \end{aligned}$$

From Table 2.2 in Reichl's text, we have, at $P_0 = 1 \text{ atm}$ and $T_0 = 298 \text{ K}$,

$$\mu_{N_2O_4}^0 = 23.49 \text{ kcal/mol} \quad \mu_{NO_2}^0 = 12.39 \text{ kcal/mol}$$

Plot of $G(T, P, \xi)$ for $P = P_0 = 1 \text{ atm}$ and $T = T_0$ & $2T_0$ is shown in the figure below. Note that $R = 1.987 \times 10^{-3} \text{ kcal/K} \cdot \text{mol}$.



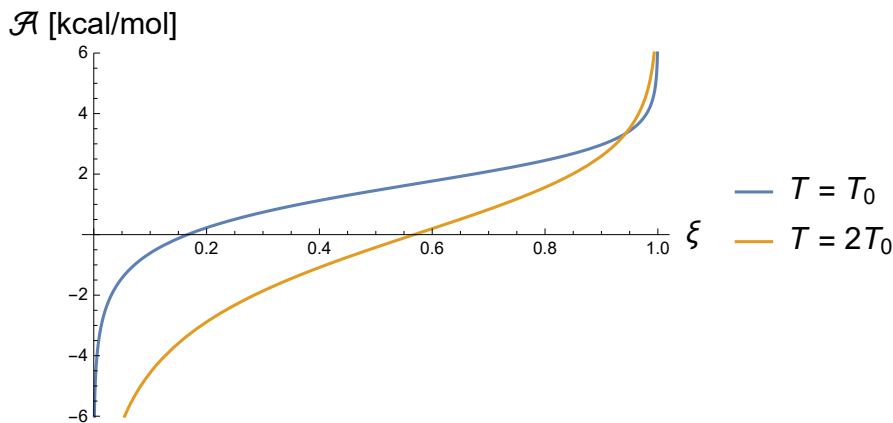
Note: This plot was misplaced in Ex.2.12 in Reichl's text.

Answer (b)

Putting (1) & (1.c-e) into (2.244a) gives

$$\begin{aligned}
 \mathcal{A}(T, P, \xi) &= -(v_{N_2O_4} + v_{NO_2}) RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + v_{N_2O_4} \mu_{N_2O_4}^0 + v_{NO_2} \mu_{NO_2}^0 + RT \ln (x_{N_2O_4}^{v_{N_2O_4}} x_{NO_2}^{v_{NO_2}}) \\
 &= -RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] - \mu_{N_2O_4}^0 + 2 \mu_{NO_2}^0 + RT \ln \left[\left(\frac{1-\xi}{1+\xi} \right)^{-1} \left(\frac{2\xi}{1+\xi} \right)^2 \right] \\
 &= -RT \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] - \mu_{N_2O_4}^0 + 2 \mu_{NO_2}^0 + RT \ln \left[\frac{(2\xi)^2}{(1+\xi)(1-\xi)} \right] \quad (3)
 \end{aligned}$$

Plot of $\mathcal{A}(T, P, \xi)$ for $P = P_0 = 1$ atm and $T = T_0$ & $2 T_0$ is shown in the figure below.



Note that as $\xi \rightarrow 1$, the $-RT \ln(1 - \xi)$ term dominates since $\lim_{x \rightarrow 0} \ln x = -\infty$. Hence, the $T = 2 T_0$ curve will rise to about twice the height of the $T = T_0$ one as $\xi \rightarrow 1$, contrary to the graph shown in Reichl's text.

Answer (c)

Setting in (3)

$$P = 1 \text{ atm} \quad T = 298 \text{ K}$$

and solve for ξ in

$$\mathcal{A} = 0 \quad [\text{Condition for equilibrium.}]$$

gives

$$\xi_{\text{eq}} = 0.166$$

Incidentally, solving ξ for

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = 0$$

gives the same answer, as expected [§Code].

Putting ξ_{eq} into (1c) then gives, at equilibrium,

$$n_{N_2O_4} = 0.834 \quad n_{NO_2} = 0.332$$

and

$$n = 1.166 \quad (3a)$$

Answer (d)

Since T & P are fixed, the ideal gas law gives

$$\frac{V}{n} = \text{const} \rightarrow \frac{V_0}{1} = \frac{V}{1.166} \quad [(3a) \text{ used.}]$$

$$\therefore V = 1.166 V_0$$

Answer (e)

Setting in (2.250)

$$P = P_0 = 1 \text{ atm} \quad T = T_0 = 298 \text{ K}$$

$$\nu_{N_2O_4} = -1 \quad \nu_{NO_2} = 2 \quad \nu_t = 1$$

gives

$$\begin{aligned} \left(\frac{\partial H}{\partial \xi} \right)_{T,P} &= \frac{5}{2} R T_0 - R T_0 \ln \left(\frac{x_{NO_2}^2}{x_{N_2O_4}} \right) \\ &= \frac{5}{2} R T_0 - R T_0 \ln \left(\frac{(0.332/1.166)^2}{0.834/1.166} \right) \quad [(3a) \text{ used.}] \\ &= 4.677 R T_0 \\ &= 2.770 \text{ kcal/mol} \end{aligned}$$

Code

Note: graphic outputs are all removed to save storage space.

(* [R] = kcal/K·mol *)

R = 1.987 × 10⁻³; T0 = 298;

μ1 = 12.39; μ2 = 23.49;

(* Temperature T is in units of T0=298K *)

$$G[\xi_, T_] := - (1 + \xi) R T T_0 \text{Log}[T^{5/2}] + (1 - \xi) \mu_2 + 2 \xi \mu_1 + R T T_0 \text{Log} \left[\frac{(1 - \xi)^{1-\xi}}{(1 + \xi)^{1+\xi}} (2 \xi)^{2 \xi} \right]$$

(* Plot of $G(\xi)$ *)

```
Plot[{G[ξ, 1], G[ξ, 2]}, {ξ, 0, 1},
      PlotRange → {Automatic, {19, 25}},
      AxesLabel → {"ξ", "G [kcal]"},
      PlotLegends → {"T = T0", "T = 2T0"}]
```

$$A[\xi_-, T_-] := -RT T_0 \text{Log}[T^{5/2}] - \mu_2 + 2 \mu_1 + RT T_0 \text{Log}\left[\frac{1}{(1+\xi)(1-\xi)} (2\xi)^2\right]$$

(* Plot of $\mathcal{A}(\xi)$ *)

```
Plot[{A[ξ, 1], A[ξ, 2]}, {ξ, 0, 1},
      PlotRange → {Automatic, 6 {-1, 1}},
      AxesLabel → {"ξ", "A [kcal/mol]"},
      PlotLegends → {"T = T0", "T = 2T0"}]
```

(* ξ_{eq} *)

```
NSolve[A[ξ, 1] == 0, ξ]
```

Solve: Solve was unable to solve the system with inexact coefficients. The answer was obtained by solving a corresponding exact system and numericizing the result.

```
{{ξ → -0.165896}, {ξ → 0.165896}}
```

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0$$

```
NSolve[∂ξG[ξ, 1] == 0, ξ, Reals]
```

```
{{ξ → 0.165896}}
```

$$\left(\frac{\partial H}{\partial \xi}\right)_{T,P}$$

$$\frac{5}{2} - \text{Log}\left[\frac{(0.332/1.166)^2}{0.834/1.166}\right]$$

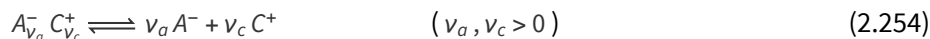
```
4.6773
```

```
% RT0
```

```
2.76955
```

S2.E. The Thermodynamics of Electrolytes

An **electrolyte** is a dilute solution (salt + water) in which the solute (salt) dissociates into charged ions via the reaction



where A^- & C^+ are called the **anion** & **cation**, respectively.

The condition for equilibrium is [see (2.238-9)]

$$\mathcal{A} = -\mu_{ac} + v_a \mu_a^e + v_c \mu_c^e = 0 \quad (2.255)$$

where the **electrochemical potential** μ_j^e is the average energy required to add 1 mole of type j (charged) ions to the system, i.e., it is the chemical potential for charged particles. For ions with valence (or charge in units of the proton charge) z_j ,

$$\mu_j^e = \mu_j + z_j F \phi \quad [\text{See (3) of Ex.2.7 in §2.F.4.}] \quad (2.255a)$$

where ϕ is the electric potential and F is the **Faraday** (amount of charge in 1 mole of protons).

Since the salt is neutral, we have

$$v_a z_a + v_c z_c = 0 \quad (2.256)$$

Experiments show that the chemical potential of salt in aqueous solution takes the form

$$\mu_{ac}(T, P, x_{ac}) \approx \mu_{ac}^0(T, P) + RT \ln \alpha_{ac} \quad (2.257)$$

where

$$\begin{aligned} \mu_{ac}^0(T, P) &= \lim_{x_{ac} \rightarrow 1} \mu_{ac}(T, P, x_{ac}) \\ &= \text{chemical potential of pure salt.} \end{aligned}$$

The **activity** α_{ac} will be defined shortly.

In the limit that the salt and water have no effect on each other, the Gibbs energy simplifies to

$$G^0(T, P, n_{ac}, n_w) = n_{ac} \mu_{ac}^0(T, P) + n_w \mu_w^0(T, P) \quad (2.258)$$

where $\mu_w^0(T, P)$ is the chemical potential for pure water.

Hence,

$$\begin{aligned} G &= n_{ac} \mu_{ac} + n_w \mu_w && [(2.107) \text{ of §2.F.4 used. }] \\ &= G_0 + n_{ac} (\mu_{ac} - \mu_{ac}^0) + n_w (\mu_w - \mu_w^0) && [(2.258) \text{ used. }] \\ &= G_0 + n_{ac} RT \ln \alpha_{ac} + n_w (\mu_w - \mu_w^0) && [(2.257) \text{ used. }] \end{aligned} \quad (2.259)$$

Generalizing (2.257) to the case for ions with (2.255a) gives

$$\mu_a^e(T, P, x_{ac}) \approx \mu_a^0(T, P) + RT \ln \alpha_a + z_a F \phi \quad (2.262)$$

$$\mu_c^e(T, P, x_{ac}) \approx \mu_c^0(T, P) + RT \ln \alpha_c + z_c F \phi \quad (2.263)$$

Putting these and (2.257) into the condition for equilibrium (2.255) gives

$$\begin{aligned} \mu_{ac}^0 + RT \ln \alpha_{ac} &= v_a \mu_a^0 + v_c \mu_c^0 + RT (v_a \ln \alpha_a + v_c \ln \alpha_c) + (v_a z_a + v_c z_c) F \phi \\ &= v_a \mu_a^0 + v_c \mu_c^0 + RT (v_a \ln \alpha_a + v_c \ln \alpha_c) && [(2.256) \text{ used. }] \end{aligned}$$

Since this holds for arbitrary T , we have

$$\mu_{ac}^0 = v_a \mu_a^0 + v_c \mu_c^0 \quad (2.261a)$$

and

$$\ln \alpha_{ac} = \nu_a \ln \alpha_a + \nu_c \ln \alpha_c \quad (2.261)$$

$$\rightarrow \alpha_{ac} = \alpha_a^{\nu_a} \alpha_c^{\nu_c} \quad (2.260)$$

It is found experimentally that for dilute solutions,

$$\alpha_j \approx f_j c_j \quad (2.260a)$$

where $c_j = \frac{n_j}{V}$ is the concentration and f_j is the **activity coefficient** for type j ions. Furthermore,

$$\lim_{c_j \rightarrow 0} f_j \rightarrow 1 \quad (2.260b)$$

Solutions in which

$$f_j = 1 \quad \forall j$$

are said to be **ideal**.

For ideal solutions, (2.262-3) simplify to

$$\mu_a^e(T, P, x_{ac}) \approx \mu_a^0(T, P) + RT \ln c_a + z_a F \phi \quad (2.264)$$

$$\mu_c^e(T, P, x_{ac}) \approx \mu_c^0(T, P) + RT \ln c_c + z_c F \phi \quad (2.265)$$

Changes in the Gibbs energy for a solution carrying the reaction (2.254) are given by [see (2.236)]

$$dG = -SdT + VdP + \mu_{ac} dn_{ac} + \mu_a^e dn_a + \mu_c^e dn_c + \mu_w dn_w \quad (2.266)$$

with

$$\frac{dn_{ac}}{-1} = \frac{dn_a}{\nu_a} = \frac{dn_c}{\nu_c} = d\xi$$

Ex.2.12.

A vessel held at constant T and P is separated into two compartments, I & II, by a membrane. Each compartment contains a well-stirred dilute solution of a solute and a solvent. The membrane is permeable to the solute but not the solvent.

Compute the ratios of the concentrations of solute in the compartments for the following two cases.

- The solute is uncharged, but the solvents in the compartments are different.
- The solute is charged, and the solvents in the compartments are the same.
But the fluids in the compartments are maintained at different electric potentials.

Answer (a)

For uncharged solute in an ideal solution, the chemical potential is given by [see (2.257)],

$$\mu_{sj} = \mu_s^0 + RT \ln \alpha_{sj} \quad j = I, II$$

where c_{sj} the concentration of the solute in compartment j and

$$\mu_s^0 = \lim_{c_{sj} \rightarrow 1} \mu_{sj} = \text{chemical potential of pure solute}$$

The condition for equilibrium is

$$\mu_{sI} = \mu_{sII}$$

$$\rightarrow \alpha_{sI} = \alpha_{sII} \rightarrow f_I c_{sI} = f_{II} c_{sII} \quad (1)$$

i.e.,

$$\frac{c_{sI}}{c_{sII}} = \frac{f_{II}}{f_I} \quad (2)$$

The ratio $\beta_s = \frac{c_{sI}}{c_{sII}}$ is called the **partition coefficient**.

Answer (b)

For charged solute in an ideal solution, the chemical potential is given by [see (2.262-3)],

$$\mu_{sj} = \mu_s^0 + RT \ln \alpha_{sj} + z_s F \phi_j \quad j = I, II$$

where ϕ_j is the electric potential in compartment j .

The condition for equilibrium is

$$\mu_{sI} = \mu_{sII}$$

$$\rightarrow RT \ln \alpha_{sI} + z_s F \phi_I = RT \ln \alpha_{sII} + z_s F \phi_{II} \quad (3)$$

Since the solvents are the same in both compartments, so are the activity coefficients f_j . (3) thus gives

$$RT \ln \frac{c_I}{c_{II}} = z_s F (\phi_{II} - \phi_I)$$

$$\rightarrow \frac{c_{sI}}{c_{sII}} = \exp\left(\frac{z_s F \Delta \phi}{RT}\right) \quad \Delta \phi = \phi_{II} - \phi_I \quad (3a)$$

so that solute concentration is higher where ϕ is lower.

The potential difference required to maintain the concentration difference,

$$\Delta \phi = \frac{RT}{z_s F} \ln \frac{c_I}{c_{II}} \quad (4)$$

is called the **Nernst potential**.