

## Special Section 2

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## **S2.A. Cooling and Liquefactions of Gases**

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

Consider the adiabatic free expansion of a gas for which

$$\Delta Q = \Delta W = \Delta n = \Delta U = 0$$

During the expansion, the gas is not in equilibrium so that thermodynamical analysis is applicable only to the initial and final equilibrium states. On the reversible path linking these 2 states, we have

$$[dU]_n = 0 = \left(\frac{\partial U}{\partial T}\right)_{v_n} dT + \left(\frac{\partial U}{\partial V}\right)_{v_n} dV \quad (2.188)$$

$$\Rightarrow dT = -\frac{\left(\frac{\partial U}{\partial V}\right)_{T_n} dV}{\left(\frac{\partial U}{\partial T}\right)_{v_n}} = \left(\frac{\partial T}{\partial V}\right)_{U_n} dV \quad (2.189)$$

The quantity

$$\left(\frac{\partial T}{\partial V}\right)_{U_n} = -\frac{1}{C_{v_n}} \left(\frac{\partial U}{\partial V}\right)_{T_n}$$

is called the **Joule coefficient**. From

$$dU = TdS - PdV + \mu dn$$

and using the diagram  $\begin{matrix} -P & T \\ S & V \end{matrix}$ , we have

$$\left(\frac{\partial U}{\partial V}\right)_{T_n} = T \left(\frac{\partial S}{\partial V}\right)_{T_n} - P = T \left(\frac{\partial P}{\partial T}\right)_{v_n} - P \quad (2.190)$$

For an ideal gas,  $PV = nRT$ , we have

$$\left(\frac{\partial U}{\partial V}\right)_{T_n} = T \frac{nR}{V} - P = P - P = 0 \quad \Rightarrow \quad \left(\frac{\partial T}{\partial V}\right)_{U_n} = 0$$

and there is no temperature change during a free expansion.

For a van der Waals gas

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad \Rightarrow \quad P = -\frac{an^2}{V^2} + \frac{nRT}{V - nb} \quad (2.190a)$$

so that

$$\left(\frac{\partial U}{\partial V}\right)_{T_n} = T \frac{nR}{V - nb} - P = \frac{an^2}{V^2} \quad (2.191)$$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_{U_n} = -\frac{an^2}{C_{v_n} V^2} \quad (2.191a)$$

To find  $C_{v_n}$ , we start with

$$\left(\frac{\partial C_{v_n}}{\partial V}\right)_{T_n} = \left(\frac{\partial}{\partial V} \left( T \frac{\partial S}{\partial T} \right)_{v_n} \right)_{T_n} = T \left( \frac{\partial}{\partial T} \left( \frac{\partial S}{\partial V} \right)_{T_n} \right)_{v_n} = T \left( \frac{\partial^2 P}{\partial T^2} \right)_{v_n} \quad (2.192)$$

Now, from (2.190a), we have

$$\left(\frac{\partial P}{\partial T}\right)_{v_n} = \frac{nR}{V-nb} \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_{v_n} = 0$$

so that by (2.192), we have

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

Since  $C_{v_n}$  contains no volume correction, it is thermodynamically consistent for it to have the same value as the ideal gas. Neglecting any contributions from internal

degrees of freedom, we have  $C_{v_n} = \frac{3}{2}nR$ . Eq(2.191a) thus becomes

$$\left(\frac{\partial T}{\partial V}\right)_{u_n} = -\frac{2an}{3RV^2} \quad (2.194)$$

Putting this into (2.189) gives

$$dT = -\frac{2an}{3RV^2}dV$$

$$\Rightarrow T_f - T_i = -\frac{2an}{3R} \int_{V_i}^{V_f} \frac{dV}{V^2} = \frac{2an}{3R} \left( \frac{1}{V_f} - \frac{1}{V_i} \right) \quad (2.196)$$

$$\text{or} \quad \Delta T = -\frac{2an}{3RV_f V_i} \Delta V$$

so that there is cooling for free expansion. However, the effect is quite small.

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

## S2.B. Entropy of Mixing and the Gibbs Paradox

Since entropy is a measurement of disorder, it should increase in the mixing of distinguishable substances. Consider an ideal gas of volume  $V$ , temperature  $T$  and consisting of  $n_j$  moles of type  $j$  molecules with  $j = 1, \dots, m$ . The equation of state is

$$P = \frac{nRT}{V} = \sum_{j=1}^m n_j \frac{RT}{V} = \sum_{j=1}^m P_j \quad (2.210)$$

where

$$n = \sum_{j=1}^m n_j \quad P_j = n_j \frac{RT}{V} \quad (2.211)$$

The molar fraction of type  $j$  molecules is defined as

$$x_j \equiv \frac{n_j}{n} = \frac{P_j}{P} \quad (2.212)$$

Consider now the Gibbs free energy  $G = G(T, P, \{n_j\})$  with

$$dG = -SdT + VdP + \sum_{j=1}^m \mu_j dn_j \quad (2.213)$$

From eq(2) of Exercise 2.3 and eq(2.107) we see that for a pure gas

$$G(T, P, n) = -nRT \ln \left( \frac{T^{5/2}}{P} \right) + G^{(0)} \quad (2.214)$$

where  $G^{(0)}$  is some constant.

For the case of  $m$  types of molecules, we begin by putting each type of molecules in its own compartment with the same overall temperature  $T$  and pressure  $P$ . The total Gibbs free energy is therefore just the sum of the energies of  $m$  pure phase compartments, i.e.,

$$\begin{aligned} G_I(T, P, \{n_j\}) &= -\sum_{j=1}^m n_j RT \ln \left( \frac{T^{5/2}}{P} \right) + G_I^{(0)} \quad (2.215) \\ &= -nRT \ln \left( \frac{T^{5/2}}{P} \right) + G_I^{(0)} \end{aligned}$$

where  $G_I^{(0)}$  is a constant. If the walls of the compartments are now removed, the gases will mix while keeping the overall temperature  $T$  and pressure  $P$  unchanged. The total Gibbs free energy is again the sum of the energies of  $m$  pure phase gases but of partial pressures given by (2.211), i.e.,

$$G_F(T, P, \{n_j\}) = -\sum_{j=1}^m n_j RT \ln \left( \frac{T^{5/2}}{P_j} \right) + G_F^{(0)} \quad (2.216a)$$

where  $G_F^{(0)}$  is a constant. Now, (2.216a) – (2.215) gives

$$\begin{aligned} \Delta G = G_F - G_I &= \sum_{j=1}^m n_j RT \ln \left( \frac{P_j}{P} \right) + G_F^{(0)} - G_I^{(0)} \\ &= \sum_{j=1}^m n_j RT \ln x_j + G_F^{(0)} - G_I^{(0)} \end{aligned} \quad (2.217)$$

The entropy of mixing is therefore

$$\Delta S_{mix} = -\sum_{j=1}^m n_j R \ln x_j \quad (2.218)$$

For  $m = 1$ , we have  $x_1 = 1$  and  $\Delta S_{mix} = 0$  as it should be.

For  $m = 2$  and  $n_1 = n_2 = 1$ , we have  $x_1 = x_2 = \frac{1}{2}$  so that  $\Delta S_{mix} = 2R \ln 2$ .

Eq(2.218) seems reasonable as long as the gases to be mixed are distinct. However, it also gives a finite entropy increase for the mixing of identical gases, which is absurd.

This is called the **Gibbs paradox** and can be resolved only by introducing the indistinguishability of identical particles in quantum mechanics.

## **S2.C. Osmotic Pressure in Dilute Solutions**



## **S2.D. The Thermodynamics of Chemical Reactions**

S2.D.1. [The Affinity](#)

S2.D.2. [Stability](#)

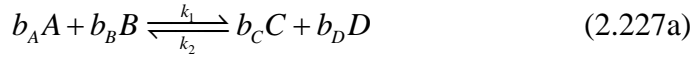
## S2.D.1. The Affinity

S2.D.1.1. [Degree of Reaction](#)

S2.D.1.2. [Gibbs Free Energy](#)

### S2.D.1.1. Degree of Reaction

Consider a chemical reaction of the form



where  $k_i$  is the **rate constant** equal to the probability per unit time that the indicated reaction can take place. Each  $b_j \geq 0$  is called a **stoichiometric coefficient** and is proportional to the number  $N_j$  of the  $j$ th kind of molecules required in the reaction.

The reaction rate of (2.227) is defined as

$$\frac{dN_A}{dt} = -k_1 N_A^{b_A} N_B^{b_B} + k_2 N_C^{b_C} N_D^{b_D} \quad (2.228a)$$

One can write (2.227a) as

$$\pm(b_A A + b_B B - b_C C - b_D D) = 0$$

or more generally,

$$\sum_i \nu_i X_i = 0 \quad (2.227b)$$

where  $X_i$  stand for the chemical substances and  $\nu_i = \pm b_i$  so that the changes in the numbers of molecules are given by

$$\Delta N_i = \lambda \nu_i \quad \forall i \quad (2.227c)$$

where  $\lambda > 0$  is some constant.

As an example, the reaction (2.227a) is written as

$$\nu_A A + \nu_B B + \nu_C C + \nu_D D = 0$$

or, to preserve the structure of (2.227a),

$$-\nu_A A - \nu_B B = \nu_C C + \nu_D D \quad (2.227)$$

For the reaction ( $k_1$ ) going to the right, we have

$$\begin{aligned} \nu_A, \nu_B < 0 \quad \text{and} \quad \nu_C, \nu_D > 0 \\ \frac{\Delta n_A}{\nu_A} = \frac{\Delta n_B}{\nu_B} = \frac{\Delta n_C}{\nu_C} = \frac{\Delta n_D}{\nu_D} = \Delta \xi \end{aligned} \quad (2.235)$$

where  $\xi$  is called the **degree of reaction**. Thus, to consume  $n_A = b_A n_0 = -\nu_A n_0$  moles of A, the resultant changes in the numbers of moles of the substances are

$$\Delta n_A = -n_A = \nu_A n_0$$

$$\Delta n_B = \frac{\nu_B}{\nu_A} \Delta n_A = \nu_B n_0 = -b_B n_0$$

$$\Delta n_C = \frac{\nu_C}{\nu_A} \Delta n_A = \nu_C n_0 = b_C n_0$$

$$\Delta n_D = \frac{\nu_D}{\nu_A} \Delta n_A = \nu_D n_0 = b_D n_0$$

If, initially, the numbers of moles of the substances are

$$n_A = -\nu_A n_0$$

$$n_B = -\nu_B n_0 + n_B''$$

$$n_C = \nu_C n_0'$$

$$n_D = \nu_D n_0' + n_D''$$

the reaction will be completed when the numbers of moles of the substances become

$$n_A = 0$$

$$n_B = n_B''$$

$$n_C = \nu_C (n_0 + n_0')$$

$$n_D = \nu_D (n_0 + n_0') + n_D''$$

### S2.D.1.2. Gibbs Free Energy

With the help of (2.235), the differential of the Gibbs energy  $G = G(T, P, \{n_j\})$

becomes

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

where  $m$  is the number of chemical species in the reaction and  $A$  is the affinity defined by

$$A \equiv \sum_{j=1}^m \mu_j \nu_j = \left( \frac{\partial G}{\partial \xi} \right)_{TP} \quad (2.238,7)$$

At chemical equilibrium where  $T$  and  $P$  are constant,  $G$  is a minimum. Hence

$$A^0 = \left( \frac{\partial G}{\partial \xi} \right)_{TP}^0 = 0 \quad (2.239)$$

where the superscript 0 denotes an equilibrium value. In other words, the condition for chemical equilibrium is

$$A = \sum_{j=1}^m \mu_j \nu_j = 0 \quad (2.239a)$$

Now, the fact that  $G$  is a minimum at equilibrium means that in the approach to equilibrium,  $dG < 0$ . To be more precisely, a spontaneous reaction must obey

$$[dG]_{TP} = \left( \frac{\partial G}{\partial \xi} \right)_{TP} d\xi = Ad\xi < 0 \quad (2.240)$$

Using the convention that  $d\xi < 0$  if the reaction (2.227) goes to the right, (2.240) then implies  $A > 0$ . Conversely, if the reaction goes to the left,  $d\xi > 0$  and  $A < 0$ .

If there are  $r$  reactions involving  $m$  chemical species, there will be  $r$  degree of reactions  $\xi_k$  defined by

$$d\xi_k = \frac{[dn_j]_k}{\nu_{jk}} \quad \text{with } k = 1, \dots, r \text{ and } j = 1, \dots, m$$

where  $[dn_j]_k$  is the change of  $n_j$  in the reaction  $k$  and  $\nu_{jk}$  is the (signed)

stoichiometric coefficient of species  $j$  in the reaction  $k$ . Since

$$dn_j = \sum_{k=1}^r [dn_j]_k \quad \text{for } j = 1, \dots, m$$

we have

$$dn_j = \sum_{k=1}^r \nu_{jk} d\xi_k \quad \text{for } j = 1, \dots, m \quad (2.241)$$

According to (2.214) [see section S2.B], the chemical potential of the  $j$ th species in a mixture of ideal gases can be written as

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

where  $P_j$  is its partial pressure and the subscript 0 denotes some convenient

reference state. Some values of  $\mu^0$  at atmospheric pressure and room temperature are listed in table 2.2. In terms of (2.242), the Gibbs free energy can be written as

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

where  $x_j = \frac{n_j}{n} = \frac{P_j}{P}$  with  $P$  being the total pressure and  $n$  the total number of moles

of gases [see 2.212]. Note that we can write

$$\sum_{j=1}^m n_j \ln x_j = \sum_{j=1}^m \ln x_j^{n_j} = \ln \left( \prod_{j=1}^m x_j^{n_j} \right)$$

so that, for example, the Gibbs free energy for the reaction (2.227) is

$$G(T, P, \xi) = \sum_{j=1}^m n_j \mu_j^0(T_0, P_0) - RTn \ln \left[ \left( \frac{T}{T_0} \right)^{5/2} \left( \frac{P_0}{P} \right) \right] \\ + RT \ln \left( x_A^{n_A} x_B^{n_B} x_C^{n_C} x_D^{n_D} \right) \quad (2.243)$$

Similarly, the affinity can be written as

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

with

$$\sum_{j=1}^m \nu_j \ln x_j = \sum_{j=1}^m \ln x_j^{\nu_j} = \ln \left( \prod_{j=1}^m x_j^{\nu_j} \right)$$

which, for the reaction (2.227), becomes

$$\sum_{j=1}^m \nu_j \ln x_j = \ln \left( x_A^{\nu_A} x_B^{\nu_B} x_C^{\nu_C} x_D^{\nu_D} \right) = \ln \left( \frac{x_C^{b_C} x_D^{b_D}}{x_A^{b_A} x_B^{b_B}} \right) \quad (2.244b)$$

At equilibrium,  $A = 0$  so that (2.244a) becomes

$$\ln \left( \frac{x_C^{b_C} x_D^{b_D}}{x_A^{b_A} x_B^{b_B}} \right) = -\frac{1}{RT} \sum_{j=1}^m \nu_j \mu_j^0(T_0, P_0) + \sum_{j=1}^m \nu_j \ln \left[ \left( \frac{T}{T_0} \right)^{5/2} \left( \frac{P_0}{P} \right) \right] \quad (2.245)$$

which is one form of the **law of mass reaction**. [see Exercise 2.11]

## S2.D.2. Stability

Since, at equilibrium,  $G = G(T, P, \xi)$  is a minimum for fixed  $T$  and  $P$ , we have

$$\left(\frac{\partial G}{\partial \xi}\right)_{TP}^0 = A^0 = 0 \quad (2.246)$$

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

From the fundamental equation

$$G = H - TS = U + PV - TS$$

we have, from (2.246),

$$\begin{aligned} 0 &= \left(\frac{\partial G}{\partial \xi}\right)_{TP}^0 = \left(\frac{\partial H}{\partial \xi}\right)_{TP}^0 - T \left(\frac{\partial S}{\partial \xi}\right)_{TP}^0 \\ \Rightarrow \left(\frac{\partial H}{\partial \xi}\right)_{TP}^0 &= T \left(\frac{\partial S}{\partial \xi}\right)_{TP}^0 \quad (2.248) \end{aligned}$$

$$\begin{aligned} &= -T \left(\frac{\partial}{\partial \xi} \left(\frac{\partial G}{\partial T}\right)_{P\xi}\right)_{TP}^0 = -T \left(\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial \xi}\right)_{PT}\right)_{P\xi}^0 \\ &= -T \left(\frac{\partial A}{\partial T}\right)_{P\xi}^0 \quad (2.249) \end{aligned}$$

The term  $\left(\frac{\partial H}{\partial \xi}\right)_{TP}^0$  is called the **heat of reaction**. It is positive (negative) for endothermic (exothermic) reactions.

For an ideal gas reaction, we can use (2.244a) in (2.249) to get

$$\left(\frac{\partial H}{\partial \xi}\right)_{TP}^0 = RT \sum_{j=1}^m \nu_j \ln \left[ \left(\frac{T}{T_0}\right)^{5/2} \left(\frac{P_0}{P}\right) \right] + \frac{5}{2} RT \sum_{j=1}^m \nu_j + RT \ln \left( \prod_{j=1}^m x_j^{\nu_j} \right) \quad (2.250)$$

$$= RT \sum_{j=1}^m \nu_j \left\{ \frac{5}{2} + \ln \left[ \left(\frac{T}{T_0}\right)^{5/2} \left(\frac{P_0}{P}\right) \right] \right\} + RT \ln \left( \prod_{j=1}^m x_j^{\nu_j} \right) \quad (2.250a)$$

The last term is due the entropy of mixing [cf (2.218) of section S2.B] and, for the



case where the total number of particles remains unchanged, i.e.,

$$dn = \sum_{j=1}^m v_j d\xi = 0 \quad \Rightarrow \quad \sum_{j=1}^m v_j = 0$$

it is the only contribution.

## **S2.E. The Thermodynamics of Electrolytes**