

THERMODYNAMICS OF IRREVERSIBLE PROCESSES APPLIED TO THERMAL TRANSPIRATION

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(Communicated by B. N. Srivastava, F.N.I.)

(Received November 23, 1954 ; read March 4, 1955)

1. INTRODUCTION

A large number of non-equilibrium phenomena have been successfully treated by the thermodynamics of irreversible processes (Denbigh, 1951 ; de Groot, 1952). Recently the Soret-effect in certain binary mixtures has been interpreted in terms of non-equilibrium thermodynamic functions such as heats of transfer (Rutherford and Drickamer, 1954). In previous communications (Srivastava, Rastogi and Varma, 1954 ; Rastogi and Srivastava, 1955) expressions have been deduced for thermal effusion and thermo-molecular pressure effect for species involving isomeric reactions or the reactions of the type $X_n \rightleftharpoons nX$. Expressions for the chemical affinity and the deviation in concentration from the equilibrium values have been derived for each chamber in the steady state. In the present paper we propose to extend the treatment to the reaction of the type $xA \rightleftharpoons yB + zC$, which is more common.

2. ENTROPY PRODUCTION AND THE STATIONARY STATE OF THE FIRST ORDER

Our system consists of two chambers, I and II, communicating with each other through a narrow opening or a capillary. The two chambers are maintained at different temperatures, chamber II being maintained at a higher temperature. We suppose that the system contains a mixture of species A , B and C , amongst which the reaction $xA \rightleftharpoons yB + zC$ takes place, where x , y and z are the stoichiometric numbers. The superscripts I and II refer to the quantities in the corresponding chambers. Following the terminology as used in previous papers, we get the following expression for the entropy production :—

$$\sigma = \frac{d_i S}{dt} = - (\Delta T/T^2) J_u - \Delta(\mu_1/T) J_1 - \Delta(\mu_2/T) J_2 - \Delta(\mu_3/T) J_3 \\ + (A^I/T^I) J_I + (A^{II}/T^{II}) J_{II} \dots \dots \dots (1)$$

where Δ refers to the difference of the quantity in the two chambers, and the subscripts 1, 2 and 3 refer respectively to the chemical species A , B and C respectively. The respective flows are defined as follows :—

$$J_1 = - \sum_{k=1}^3 L_{1k} \Delta(\mu_k/T) - L_{1u} (\Delta T/T^2) \\ J_2 = - \sum_{k=1}^3 L_{2k} \Delta(\mu_k/T) - L_{2u} (\Delta T/T^2)$$

$$\begin{aligned}
 J_3 &= - \sum_{k=1}^3 L_{3k} \Delta(\mu_k/T) - L_{3u} (\Delta T/T^2) \\
 J_u &= - \sum_{k=1}^3 L_{uk} \Delta(\mu_k/T) - L_{uu} (\Delta T/T^2) \\
 J_I &= L_{cc} (A^I/T^I) \\
 J_{II} &= L'_{cc} (A^{II}/T^{II}) \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (2)
 \end{aligned}$$

The affinity A is defined by the relation $A = x\mu_1 - y\mu_2 - z\mu_3$, where μ is the chemical potential. In the above expressions L_{ik} and L_{uk} represent the phenomenological coefficients. L_{cc} and L'_{cc} are the coefficients associated with the chemical reaction rate J .

Inserting equation (2) in equation (1) and making use of Onsager reciprocal relations we obtain

$$\begin{aligned}
 \sigma &= L_{11} \{ \Delta(\mu_1/T) \}^2 + L_{22} \{ \Delta(\mu_2/T) \}^2 + L_{33} \{ \Delta(\mu_3/T) \}^2 + L_{uu} \{ \Delta T/T \}^2 \\
 &+ 2L_{12} \Delta(\mu_1/T) \cdot \Delta(\mu_2/T) + 2L_{13} \Delta(\mu_1/T) \cdot \Delta(\mu_3/T) + 2L_{23} \Delta(\mu_2/T) \cdot \Delta(\mu_3/T) \\
 &+ 2L_{1u} \Delta(\mu_1/T) \cdot (\Delta T/T^2) + 2L_{2u} \Delta(\mu_2/T) \cdot (\Delta T/T^2) + 2L_{3u} \Delta(\mu_3/T) (\Delta T/T^2) \\
 &+ L_{cc} (A^I/T^I)^2 + L'_{cc} (A^{II}/T^{II})^2 \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (3)
 \end{aligned}$$

We shall consider the stationary state of the first order when ΔT is kept constant. Corresponding to each of the independent forces, $\Delta(\mu_1/T)$, $\Delta(\mu_2/T)$, $\Delta(\mu_3/T)$ and (A^I/T^I) we have the conditions

$$\frac{\delta\sigma}{\delta\Delta(\mu_1/T)} = 0; \quad \frac{\delta\sigma}{\delta\Delta(\mu_2/T)} = 0; \quad \frac{\delta\sigma}{\delta\Delta(\mu_3/T)} = 0; \quad \frac{\delta\sigma}{\delta(A^I/T^I)} = 0 \quad \dots \quad (4)$$

But these forces are related by the relation

$$A^{II}/T^{II} = A^I/T^I + x \cdot \Delta(\mu_1/T) - y \cdot \Delta(\mu_2/T) - z \cdot \Delta(\mu_3/T) \quad \dots \quad (5)$$

Using equations (4) and (5) we obtain the following set of relations from equation (3) :—

$$\left. \begin{aligned}
 L_{11} \Delta(\mu_1/T) + L_{12} \Delta(\mu_2/T) + L_{13} \Delta(\mu_3/T) + L_{1u} (\Delta T/T^2) - L_{cc} \cdot x \cdot \frac{A^I}{T^I} &= 0 \\
 L_{12} \Delta(\mu_1/T) + L_{22} \Delta(\mu_2/T) + L_{23} \Delta(\mu_3/T) + L_{2u} (\Delta T/T^2) + L_{cc} \cdot y \cdot \frac{A^I}{T^I} &= 0 \\
 L_{13} \Delta(\mu_1/T) + L_{23} \Delta(\mu_2/T) + L_{33} \Delta(\mu_3/T) + L_{3u} (\Delta T/T^2) + L_{cc} \cdot z \cdot \frac{A^I}{T^I} &= 0 \\
 L_{cc} \cdot A^I/T^I + L'_{cc} \cdot A^{II}/T^{II} &= 0
 \end{aligned} \right\} \quad (6)$$

For such a three-component system the chemical potential may be written in the form

$$\Delta(\mu_k/T) = -h_k (\Delta T/T^2) + v_k (\Delta P/T) + \sum_{i=1}^2 \left(\frac{\partial \mu_k}{\partial c_i} \right) \frac{\Delta c_i}{T} \quad (k=1, 2, 3) \quad \dots \quad (7)$$

where h_k and v_k are the partial specific enthalpy and partial specific volume of the component k , and c_i is the mass fraction of the species i .

On solving equations (6) we obtain

$$\frac{\Delta P}{\Delta T} = \frac{1}{T(v_1 d_1 + v_2 d_2 + v_3 d_3)} \cdot [(h_1 + L_1)d_1 + (h_2 + L_2)d_2 + (h_3 + L_3)d_3] \quad \dots \quad (8)$$

$$\frac{\Delta c_1}{\Delta T} = \frac{[(h_1 + L_1)\left(v_3 \frac{\partial \mu_2}{\partial c_2} - v_2 \frac{\partial \mu_3}{\partial c_2}\right) + (h_2 + L_2)\left(v_1 \frac{\partial \mu_3}{\partial c_2} - v_3 \frac{\partial \mu_2}{\partial c_2}\right) + (h_3 + L_3)\left(v_2 \frac{\partial \mu_1}{\partial c_2} - v_1 \frac{\partial \mu_2}{\partial c_2}\right)]}{T(v_1 d_1 + v_2 d_2 + v_3 d_3)} \quad \dots \quad (9)$$

$$\frac{\Delta c_2}{\Delta T} = \frac{[(h_1 + L_1)\left(v_2 \frac{\partial \mu_3}{\partial c_1} - v_3 \frac{\partial \mu_1}{\partial c_1}\right) + (h_2 + L_2)\left(v_3 \frac{\partial \mu_1}{\partial c_1} - v_1 \frac{\partial \mu_3}{\partial c_1}\right) + (h_3 + L_3)\left(v_1 \frac{\partial \mu_2}{\partial c_1} - v_2 \frac{\partial \mu_1}{\partial c_1}\right)]}{T(v_1 d_1 + v_2 d_2 + v_3 d_3)} \quad \dots \quad (10)$$

$$\frac{A^I}{T^I} \cdot \frac{1}{\Delta T} = \frac{L'_{cc}}{L_{cc} + L'_{cc}} \cdot \frac{1}{T^2} [zL_3 + yL_2 - xL_1]; \quad \frac{A^{II}}{T^{II}} \cdot \frac{1}{\Delta T} = \frac{-L_{cc}}{L_{cc} + L'_{cc}} \cdot \frac{1}{T^2} [zL_3 + yL_2 - xL_1] \quad \dots \quad (11)$$

where

$$L_1 = \frac{(a_1 L_{1u} + b_1 L_{2u} + c_1 L_{3u})L_{cc} \cdot L'_{cc} + (a_2 L_{1u} + b_2 L_{2u} + c_2 L_{3u})(L_{cc} + L'_{cc})}{XL_{cc} \cdot L'_{cc} + Y(L_{cc} + L'_{cc})}$$

$$L_2 = \frac{(b_1 L_{1u} + e_1 L_{2u} + f_1 L_{3u})L_{cc} \cdot L'_{cc} + (b_2 L_{1u} + e_2 L_{2u} + f_2 L_{3u})(L_{cc} + L'_{cc})}{XL_{cc} \cdot L'_{cc} + Y(L_{cc} + L'_{cc})}$$

$$L_3 = \frac{(c_1 L_{1u} + f_1 L_{2u} + g_1 L_{3u})L_{cc} \cdot L'_{cc} + (c_2 L_{1u} + f_2 L_{2u} + g_2 L_{3u})(L_{cc} + L'_{cc})}{XL_{cc} \cdot L'_{cc} + Y(L_{cc} + L'_{cc})}$$

$$a_1 = z^2 L_{22} - 2yz L_{23} + y^2 L_{33}; \quad a_2 = L_{22} L_{33} - L_{23}^2$$

$$b_1 = -z^2 L_{12} + yz L_{13} - xz L_{23} + xy L_{33}; \quad b_2 = L_{13} L_{23} - L_{12} L_{33}$$

$$c_1 = yz L_{12} - y^2 L_{13} + xz L_{22} - xy L_{23}; \quad c_2 = L_{12} L_{23} - L_{13} L_{22}$$

$$e_1 = z^2 L_{11} + 2xz L_{13} + x^2 L_{33}; \quad e_2 = L_{11} L_{33} - L_{13}^2$$

$$f_1 = -yz L_{11} - xz L_{12} - xy L_{13} - x^2 L_{23}; \quad f_2 = L_{12} L_{13} - L_{11} L_{23}$$

$$g_1 = y^2 L_{11} + 2xy L_{12} + x^2 L_{22}; \quad g_2 = L_{11} L_{22} - L_{12}^2$$

$$X = -a_2 x^2 - e_2 y^2 - g_2 z^2 + 2b_2 xy + 2c_2 xz - 2f_2 yz$$

$$Y = L_{11} L_{23}^2 + L_{22} L_{13}^2 + L_{33} L_{12}^2 - L_{11} L_{22} L_{33} - L_{12} L_{13} L_{23}$$

$$d_1 = \left(\frac{\partial \mu_2}{\partial c_1} \cdot \frac{\partial \mu_3}{\partial c_2} - \frac{\partial \mu_2}{\partial c_2} \cdot \frac{\partial \mu_3}{\partial c_1} \right)$$

$$d_2 = \left(\frac{\partial \mu_3}{\partial c_1} \cdot \frac{\partial \mu_1}{\partial c_2} - \frac{\partial \mu_3}{\partial c_2} \cdot \frac{\partial \mu_1}{\partial c_1} \right)$$

$$d_3 = \left(\frac{\partial \mu_1}{\partial c_1} \cdot \frac{\partial \mu_2}{\partial c_2} - \frac{\partial \mu_1}{\partial c_2} \cdot \frac{\partial \mu_2}{\partial c_1} \right)$$

The equations (8), (9), (10) and (11) are fairly complicated and cannot be used in practice. As shown previously we can get an expression for affinity which does

not involve phenomenological coefficients. Thus, from equations (8), (9) and (10) we get

$$L_1 = T \left[\frac{\Delta P}{\Delta T} v_1 + \frac{\Delta c_1}{\Delta T} \cdot \frac{\partial \mu_1}{\partial c_1} + \frac{\Delta c_2}{\Delta T} \cdot \frac{\partial \mu_1}{\partial c_2} \right] - h_1 \quad \dots \quad (12)$$

$$L_2 = T \left[\frac{\Delta P}{\Delta T} v_2 + \frac{\Delta c_1}{\Delta T} \cdot \frac{\partial \mu_2}{\partial c_1} + \frac{\Delta c_2}{\Delta T} \cdot \frac{\partial \mu_2}{\partial c_2} \right] - h_2 \quad \dots \quad (13)$$

$$L_3 = T \left[\frac{\Delta P}{\Delta T} v_3 + \frac{\Delta c_1}{\Delta T} \cdot \frac{\partial \mu_3}{\partial c_1} + \frac{\Delta c_2}{\Delta T} \cdot \frac{\partial \mu_3}{\partial c_2} \right] - h_3 \quad \dots \quad (14)$$

Substituting the values of L_1 , L_2 and L_3 in equation (11) we obtain

$$\begin{aligned} \frac{A^I}{T^I} \cdot \frac{1}{\Delta T} = & \frac{L'_{cc}}{L_{cc} + L'_{cc}} \cdot \frac{1}{T^2} \left[T \cdot \frac{\Delta P}{\Delta T} \cdot (zv_3 + yv_2 + xv_1) + T \cdot \frac{\Delta c_1}{\Delta T} \left(z \frac{\partial \mu_3}{\partial c_1} + y \frac{\partial \mu_2}{\partial c_1} - x \frac{\partial \mu_1}{\partial c_1} \right) \right. \\ & \left. + T \cdot \frac{\Delta c_2}{\Delta T} \left(z \frac{\partial \mu_3}{\partial c_2} + y \frac{\partial \mu_2}{\partial c_2} - x \frac{\partial \mu_1}{\partial c_2} \right) - (zh_3 + yh_2 - xh_1) \right] \dots \quad (15) \end{aligned}$$

If we consider a mixture of perfect gases, the above relation may be further simplified. For then,

$$v_k = \frac{RT}{M_k \cdot P}$$

and h_k can also be evaluated. For enthalpy we have earlier (Rastogi and Srivastava, 1954) used the expression

$$h_k = \frac{5}{2} \cdot \left(\frac{RT}{M_k} \right)$$

Strictly speaking this is true for the translational component of enthalpy. Even in a monatomic gas the atoms possess internal vibrations, but the vibrational energies are almost negligible and hence the above equation is correct for at least monatomic gases, particularly at not too high temperatures. For diatomic molecules there are three degrees of freedom of translation and two of rotation about the two axes perpendicular to the line joining the atoms. If we do not take into account the structure of atoms, we have

$$h_k = \frac{7}{2} \cdot \frac{RT}{M_k}$$

Similarly for a triatomic gas we have,

$$h_k = \frac{4RT}{M_k}$$

since a triatomic molecule has three translational and three rotational degrees of freedom. In this case we do not consider the vibrational degrees of freedom since the vibrations are usually not fully excited.

Thus for diatomic molecules equation (15) yields

$$\begin{aligned} \frac{A^I}{T^I} \cdot \frac{1}{\Delta T} = & \frac{L'_{cc}}{L_{cc} + L'_{cc}} \cdot \frac{R}{T} \left[\frac{\Delta \log P}{\Delta \log T} \left(\frac{z}{M_3} + \frac{y}{M_2} - \frac{x}{M_1} \right) \right. \\ & \left. + \frac{1}{\Delta \log T} (z \Delta \log c_3 + y \Delta \log c_2 - x \Delta \log c_1) - \frac{7}{2} \left(\frac{z}{M_3} + \frac{y}{M_2} - \frac{x}{M_1} \right) \right] \quad (16) \end{aligned}$$

From the definition of affinity it follows that

$$A = RT \cdot \delta c_1 \left[\frac{x}{c_1^0} + \frac{z}{c_3^0} \right] + RT \delta c_2 \left[\frac{z}{c_3^0} - \frac{y}{c_2^0} \right] \quad \dots \quad (17)$$

for $\delta c_1 \ll c_1^0$ and $\delta c_2 \ll c_2^0$ where δc_k is the deviation in concentration in a particular chamber. Thus from equations (16) and (17) one can obtain a relation between the deviation in concentration of the respective species in a particular chamber and the temperature, pressure and the concentration prevailing in the two chambers. The above relation (16) can be easily checked provided suitable experiments are performed. In the next section equation (16) would be used to calculate the free energy change in either chamber for the thermal decomposition of deuterium iodide.

3. THERMAL DECOMPOSITION OF DEUTERIUM IODIDE

The kinetics of the reaction $2DI \rightleftharpoons D_2 + I_2$ has been recently studied (Taylor and Crist, 1941). The advantage in using this reaction is that L_{cc} and L'_{cc} can be readily calculated as the specific rate constants for both the forward and back reactions have been experimentally determined. In the following calculations experimental data for two temperatures, viz., 666.8°K. and 698.8°K. have been utilized for which the equilibrium concentration in moles/c.c. is given. We assume that chamber I is maintained at 666.8°K. and chamber II is maintained at 698.8°K. We further suppose that equilibrium concentrations and pressures are not affected significantly if the two chambers are connected by a narrow opening. For the case of thermal decomposition of deuterium iodide we shall have the following equation for affinity:—

$$\frac{A^I}{T^I} \cdot \frac{1}{\Delta T} = \frac{L'_{cc}}{L_{cc} + L'_{cc}} \cdot \frac{R}{T} \left[\left(\frac{\Delta \log P}{\Delta \log T} - \frac{7}{2} \right) \left(\frac{1}{M_3} + \frac{1}{M_2} - \frac{2}{M_1} \right) + \frac{1}{\Delta \log T} (\Delta \log c_3 + \Delta \log c_2 - 2 \Delta \log c_1) \right]$$

Here

$$\frac{L_{cc}}{L'_{cc}} = \frac{k[M_1^0]_{T^I}^2}{k'[M_1^0]_{T^{II}}^2};$$

$[M_1^0]$ represents the mass at equilibrium and k and k' are the specific rate constants for the decomposition at the two temperatures, T^I and T^{II} . The following table gives the values of affinity for different pressures and concentrations in each chamber:—

TABLE I

$T^I = 666.8^\circ\text{K.}; T^{II} = 698.8^\circ\text{K.}$

P^I (atm.)	P^{II} (atm.)	C_1^I	C_2^I	C_3^I	C_1^{II}	C_2^{II}	C_3^{II}	A (cal.)
1.099	1.333	0.857	0.00621	0.1202	0.8642	0.00771	0.1280	270.61
1.023	1.098	0.887	0.00991	0.1027	0.8816	0.00984	0.1084	63.06
1.064	1.125	0.872	0.00838	0.1200	0.8702	0.00858	0.1213	11.21
1.180	1.156	0.848	0.00630	0.1460	0.8563	0.00589	0.1362	-188.71

It is a pleasure to acknowledge the continued interest taken by Prof. A. C. Chatterji and Prof. B. N. Srivastava during the course of the investigation.

ABSTRACT

The non-equilibrium thermodynamics of thermal transpiration of species involving the reaction of the type $xA \rightleftharpoons yB + zC$ has been developed by using Onsager reciprocal relations. Expressions for affinity which do not involve phenomenological coefficients are deduced for either chamber. The equilibrium data for the thermal decomposition of deuterium iodide has been used to calculate the value of affinity in order to have an estimate of the shift from thermodynamic equilibrium.

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Issued August 12, 1955.