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John Newman
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Introduction

This material serves both as a review and as an introduction. Consequently, the readers should expect to learn this material later, and it may be useful to return to the Introduction to give them a better overall view of the subject of thermodynamics. Hopefully this review will inspire them to get on with learning the thermodynamics in the following chapters.

For a gas mixture obeying the truncated virial equation,

$$\frac{p\tilde{V}}{RT} = 1 + B'p, \quad (1)$$

where

$$B' = \sum_i \sum_j y_i y_j B'_{i,j}(T) \quad \text{and} \quad B'_{i,j} = \frac{B_{i,j}}{RT}, \quad (2)$$

the Gibbs function becomes

$$\tilde{G} = RT \ln p + RTB'p + \sum_i y_i \mu_i^*(T) + RT \sum_i y_i \ln y_i. \quad (3)$$

This formulation is important because all thermodynamic properties can be derived when the Gibbs function is expressed as a function of T , p , and n_i . This equation applies to real gases up to 10 or 20 atm and gives explicitly the dependence on T , p , and n_i . You can set $B'_{i,j}$ equal to zero if you want to recover equations for an ideal gas, but the equations retaining $B'_{i,j}$ are valuable because they reveal how real gases may or may not approach ideal-gas behavior as p approaches zero. (For example, $(\partial H / \partial p)_T$ does not approach zero for a real gas but is identically zero for an ideal gas.) On the other hand, you may want to substitute more sophisticated equations of state to give accurate treatment at pressures greater than 10 or 20 atm.

Review Questions

1. Suppose that you have been given the Gibbs function G in terms of temperature, pressure, and mole numbers as independent

variables. Describe briefly, with equations, how you would obtain the following quantities:

- a. Heat capacity, C_p .
 - b. Compressibility factor.
 - c. Equilibrium composition if it is perceived that a single chemical reaction is possible among the constituents present.
2. Reflect on the possibility of working in reverse order to infer the Gibbs function from data on the heat capacity and compressibility factor for a nonreacting system. Do you also need the results of reversible mixing experiments (such as what the Gibbs mixing rule tells you)?

The chemical potential of a component in a gas mixture can be expressed as

$$\mu_i = \mu_i^*(T) + RT \ln(py_i\phi_i), \quad (4)$$

an equation that merely *defines* the fugacity coefficient ϕ_i . Manipulation of G from Eq. 3 according to the definition of the chemical potential

$$\mu_i = \left(\frac{\partial n\tilde{G}}{\partial n_i} \right)_{T,p,n_j} \quad (5)$$

and comparison of the result with Eq. 4 permit us to write

$$\ln \phi_i = -B'p + 2p \sum_j y_j B'_{i,j}. \quad (6)$$

For a binary mixture, this takes the explicit form

$$\ln \phi_1 = p \left[y_1(2 - y_1)B'_{1,1} + 2y_2^2 B'_{1,2} - y_2^2 B'_{2,2} \right]. \quad (7)$$

Both these expressions show that ϕ_i approaches 1 as p approaches zero. Also, one sees that $\phi_i = 1$ for an ideal-gas mixture (where $B'_{i,j} = 0$).

From Eq. 4, the entropy is

$$\tilde{S} = - \left(\frac{\partial \tilde{G}}{\partial T} \right)_{p,n_i} = -R \ln p - Rp \frac{\partial(B'T)}{\partial T} - \sum_i y_i \frac{d\mu_i^*}{dT} - R \sum_i y_i \ln y_i. \quad (8)$$

The heat capacity then follows as

$$\tilde{C}_p = T \left(\frac{\partial \tilde{S}}{\partial T} \right)_{p, n_i} = -RTp \frac{\partial^2 (B'T)}{\partial T^2} - T \sum_i y_i \frac{d^2 \mu_i^*}{dT^2}. \quad (9)$$

If we let p approach zero, this equation then leads to the result

$$\frac{d^2 \mu_i^*}{dT^2} = -\frac{\tilde{C}_{pi}^*}{T}, \quad (10)$$

where \tilde{C}_{pi}^* is the low pressure limit of the molar heat capacity of a pure component. Integration of Eq. 10 to give μ_i^* from data on \tilde{C}_{pi}^* requires two integration constants to be specified. These correspond to the primary reference states for both entropy and enthalpy for each substance. For reacting systems, these two integration constants can be related back to primary reference states for the elements.

Chemical Equilibrium

Minimization of the Gibbs function for a reacting system under constraints of constant temperature and pressure leads to the general equilibrium condition:

$$\sum_i \nu_{i,\ell} \mu_i = 0, \quad (11)$$

where $\nu_{i,\ell}$ denotes the stoichiometric coefficient of species i in reaction ℓ . A separate equation of this form applies for each *independent* chemical reaction.

Substitution of Eq. 4 *immediately* yields

$$K_\ell = \prod_i (y_i p \phi_i)^{\nu_{i,\ell}}, \quad (12)$$

where

$$K_\ell = \exp \left(-\frac{\Delta G^*}{RT} \right) \quad (13)$$

and

$$\Delta G^* = \sum_i \nu_{i,\ell} \mu_i^*. \quad (14)$$

K_ℓ is called the thermodynamic equilibrium constant for the reaction and is a function of temperature only. ΔG^* is called the standard

Gibbs function change for the reaction. It should perhaps be noted that ΔG^* and μ_i^* are collections of integration constants or secondary-reference-state quantities and not actually the Gibbs function or the chemical potentials themselves. In this regard, the notation is confusing.

Based on the fundamental equation

$$\frac{d \ln K}{dT} = \frac{\Delta H^*}{RT^2},$$

we can work out the temperature dependence of the equilibrium constant:

$$\begin{aligned} \ln \frac{K}{K(T_0)} = & -\frac{\Delta H^*(T_0)}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \frac{\Delta a}{R} \left(\ln \frac{T}{T_0} + \frac{T_0}{T} - 1 \right) \\ & + \frac{(T - T_0)^2}{2RT} \left(\Delta b + \frac{\Delta c}{TT_0^2} + \frac{T + 2T_0}{3} \Delta \gamma \right), \end{aligned} \quad (15)$$

where the temperature dependence of the heat capacity at low pressure is expressed as

$$\tilde{C}_{pi}^* = a_i + b_i T + c_i / T^2 + \gamma_i T^2, \quad (16)$$

and

$$\Delta a = \sum_i \nu_{i,\ell} a_i, \quad \Delta H^* = \sum_i \nu_{i,\ell} \tilde{H}_i^*, \text{ etc.} \quad (17)$$

Equations 12 and 15 provide a rather complete account of the temperature and pressure dependence of the equilibrium composition in a system of chemically reacting gases. The description is rather good even if one does not take the trouble to estimate the fugacity coefficients and takes instead $\phi_i = 1$. The results are of industrial importance because they allow the prediction of the maximum possible conversion in a chemical reactor. Furthermore, they define the proper driving force tending to propel reactions toward equilibrium when the kinetics of the reactions are used in the design of the reactor. Fundamental data for treating a variety of important systems at various temperatures and pressures can be summarized on a single sheet, as in Table 1.

In addition to the equilibrium relations (Eq. 12) and the means for calculating the equilibrium constant (Eq. 15), it is necessary to deal with material balances or stoichiometry of the reactions in order to complete the determination of the equilibrium composition.

Table 1 Thermodynamic data for treating chemical equilibria in gas-phase systems.

	\tilde{H}_i^* $\frac{\text{kcal}}{\text{mol}}$	μ_i^* $\frac{\text{kcal}}{\text{mol}}$	a $\frac{\text{cal}}{\text{K}\cdot\text{mol}}$	$10^3 b$ $\frac{\text{cal}}{\text{K}^2\cdot\text{mol}}$	$10^{-5} c$ $\frac{\text{cal}\cdot\text{K}}{\text{mol}}$	$10^6 \gamma$ $\frac{\text{cal}}{\text{K}^3\cdot\text{mol}}$
H ₂	0	0	6.52	0.78	0.12	—
CO	-26.416	-32.78	6.79	0.98	-0.11	—
CH ₃ OH	-47.96	-38.72	4.394	24.274	—	-6.855
CO ₂	-94.051	-94.254	10.57	2.10	-2.06	—
H ₂ O	-57.796	-54.634	7.30	2.46	—	—
CH ₄	-17.88	-12.13	5.65	11.44	-0.46	—
N ₂	0	0	6.83	0.90	-0.12	—
NH ₃	-11.02	-3.94	7.11	6.00	-0.37	—
NO	21.57	20.69	7.09	0.92	-0.14	—
NO ₂	7.93	12.26	10.07	2.28	-1.67	—
N ₂ O	19.61	24.90	10.92	2.06	-2.04	—
S ₂	30.68	18.96	8.72	0.16	-0.90	—
H ₂ S	-4.93	-8.02	7.81	2.96	-0.46	—
SO ₂	-70.944	-71.748	11.04	1.88	-1.84	—
SO ₃	-94.58	-88.69	13.90	6.10	-3.22	—
HCHO	-28	-27	—	—	—	—
HNO ₃	-32.28	-17.87	12.75	—	—	—

Note: \tilde{H}_i^* and μ_i^* are given at 298.15 K.

