December, 1987] © *1987 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.,* ***60,*** *4483—4485 (1987)* 4483

Some Applications of Thermodynamic Equations on the Pressure Effect of the Chemical Reactions

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(Received August 24, 1985)

Synopsis. This paper is concerned with the theoretical derivation of the linear relationship between enthalpy and entropy for pressure change in chemical equilibria, and its application to the dissociation equilibria of some 4-substituted 1-methylpyridinium iodides in water-ethanol mixture. The isoequilibrium temperature, $\bar{\beta}$, for this system was derived to be 322 K.

In the studies of chemical equilibria and reaction kinetics in gas and liquid phases, it is better to measure the pressure effect on the system, because pressure is the conjugated thermodynamic variable of the volume which is more direct parameter than entropy conjugated to temperature. We have found experimentally the interesting fact that a linearity between enthalpy and entropy for pressure change exists in chemical equilibria and reaction rates.[1,2] B. S. El'yanov and E. M. Vasylvistskaya[3] have proved the same relationship theoretically and defined the isoequilibrium temperature, $\bar{\beta}$, under high pressure.

Theory

From the Maxwell relation of thermodynamic, we get the following equation;

$$(\partial S/\partial P)_T = -(\partial V/\partial T)_P = -V\alpha, \tag{1}$$

where α is the isobaric volume expansivity.

From the first and second laws of thermodynamics, $dH = TdS + VdP$, we obtain directly Eq. 2,

$$V = (\partial H/\partial P)_T - T(\partial S/\partial P)_T. \tag{2}$$

Substituting V in Eq. 2 into Eq. 1, we get Eq. 3,

$$(\partial H/\partial P)_T = \frac{T\alpha - 1}{\alpha}(\partial S/\partial P)_T. \tag{3}$$

On the other hand, we can define volume as

$$V = -\frac{1}{\beta}(\partial V/\partial P)_T, \tag{4}$$

where β is the isothermal compressibility.
Inserting Eq. 4 into Eq. 1 leads to

$$(\partial V/\partial P)_T = \frac{\beta}{\alpha}(\partial S/\partial P)_T. \tag{5}$$

From Eqs. 3 and 5, we obtain the following result.

$$(\partial H/\partial P)_T = \frac{T\alpha - 1}{\beta}(\partial V/\partial P)_T \tag{6}$$

Experimental

The experiments were performed in the 5 ml conductance cell which had been made to use under high pressure. A detailed explanation of the equipment and the procedures has been given in the previous papers.[4—7]

The equilibria of several 4-substituted 1-methylpyridinium iodides in ehanol-water mixture (95/5 vol%) were measured by monitoring the conductance in the range over 25—40 °C (±0.01 °C) and 1—20000 bar (±10 bar), and also by monitoring UV absorbance at the wavelength of the absorption maximum in the same range of temperature.[8,9] Purified 4-substituted 1-methylpyridinium iodides were diluted to

Table 1. Association Constants ($K \times 10^{-3}$ dm^3 mol^{-1}) of 4-Substituted 1-Methyl-pyridiniumiodides in Ethanol-Water Mixture (95/5 vol%)

Substituent	T/°C	P/bar				
		1	500	1000	1500	2000
	25	3.94±0.10	4.08±0.12	4.16±0.11	4.34±0.12	4.60±0.11
-H	30	3.26±0.08	3.35±0.09	3.45±0.10	3.57±0.09	3.79±0.10
	35	2.70±0.07	2.74±0.06	2.89±0.07	3.04±0.08	3.23±0.08
	40	2.50±0.08	2.55±0.07	2.65±0.06	2.78±0.07	2.87±0.07
	25	2.64±0.07	2.80±0.07	3.01±0.08	3.26±0.08	3.56±0.09
$-CH_3$	30	2.37±0.06	2.46±0.07	2.66±0.06	2.97±0.09	3.09±0.08
	35	2.18±0.05	2.29±0.06	2.44±0.06	2.61±0.07	2.84±0.09
	40	2.04±0.06	2.16±0.05	2.27±0.06	2.37±0.08	2.54±0.10
	25	9.61±0.24	10.5±0.26	11.6±0.29	12.8±0.25	13.9±0.32
-CN	30	7.32±0.18	8.20±0.21	9.07±0.22	9.99±0.19	10.9±0.31
	35	6.63±0.16	7.26±0.18	7.84±0.20	8.46±0.21	9.12±0.28
	40	5.45±0.14	6.18±0.15	6.78±0.21	7.38±0.18	7.89±0.19
	25	3.67±0.09	4.15±0.12	4.58±0.11	4.96±0.12	5.41±0.16
$-NH_2$	30	2.98±0.07	3.32±0.08	3.65±0.09	4.10±0.11	4.46±0.11
	35	2.61±0.07	2.86±0.08	3.23±0.08	3.56±0.09	3.74±0.12
	40	2.14±0.05	2.37±0.07	2.61±0.07	2.86±0.08	3.11±0.11

Table 2. Thermodynamic Parameters of 4-Substituted Pyridinium Iodides in Ethanol-Water Mixture (95/5%) at 30 °C and Various Pressures

Substituent	Parameter	P/bar 1	500	1000	1500	2000	Error
-H	ΔH/kcal mol^{-1}	−4.66	−4.93	−5.13	−5.27	−5.46	±0.15
	ΔS/e.u.	0.69	−0.39	−0.79	−1.12	−1.65	±0.04
	ΔV/cm^3 mol^{-1}	4.46	4.42	4.38	4.34	4.32	±0.13
-CH_3	ΔH	−3.12	−3.18	−3.32	−3.48	−3.97	±0.12
	ΔS	5.24	5.01	4.71	4.38	2.87	±0.15
	ΔV	4.44	4.42	4.41	4.40	4.39	±0.13
-CN	ΔH	−5.86	−5.92	−6.04	−6.18	−6.26	±0.18
	ΔS	−1.35	−1.62	−1.85	−2.08	−2.39	±0.06
	ΔV	6.43	6.36	6.28	6.20	6.13	±0.19
-NH_2	ΔH	−6.10	−6.14	−6.16	−6.28	−6.36	±0.18
	ΔS	−3.98	−4.02	−4.06	−4.12	−4.19	±0.13
	ΔV	5.71	5.65	5.59	5.53	5.47	±0.17

about 9.10×10^{-5}—5.10×10^{-4} mol dm^{-3} by the use of the water-ethanol mixture.

The association constants (K) of the sample determined in this way are shown in Table 1. The values of K were evaluated as the average value obtained from four measurements. Their absolute errors were about ±3%.

The values of ΔH, ΔS, and ΔV were calculated from the following equations;

$$\Delta H = -R(\partial \ln K/\partial(\frac{1}{T}))_P, \qquad (7)$$

$$\Delta S = (\Delta H - \Delta G)/T, \qquad (8)$$

$$\Delta V = -RT(\partial \ln K/\partial P)_T. \qquad (9)$$

The values of these thermodynamic parameters were shown in Table 2.

Results and Discussion

A form of $\delta\Delta H = \bar{\beta}\delta\Delta S$ with $\bar{\beta} \geqq 0$ is called an isoequilibrium relationship. A corresponding expression between the kinetcic quantities is called an isokinetic relationship.[10-12] The reason for this nomenclature is clear from the following equation;

$$\begin{aligned}\delta\Delta G &= \delta\Delta H - T\delta\Delta S,\\ &= (\bar{\beta} - T)\delta\Delta S \qquad (10)\end{aligned}$$

where the parameter, $\bar{\beta}$, has the unit of absolute temperature. If the value of $\bar{\beta}$ approaches to the experimental temperature (T), all the differences in the rate or equilibrium constants will vanish;

$$\lim_{T\to\beta} (\partial\Delta G) = 0 \qquad (11)$$

To illustrate the pressure dependence of $\delta\Delta H = \bar{\beta}\delta\Delta S$, we integrated Eq. 3 in the range from 1 to P bars assuming that the pressure dependence of $(T\alpha - 1)/\alpha$ is negligible as shown in Fig. 1, although α is slightly dependent on pressure in the liquid phase reaction;

$$(\Delta H_P - \Delta H_0) = \frac{T\alpha - 1}{\alpha}(\Delta S_P - \Delta S_0), \qquad (12)$$

where subscripts 0 and P represent 1 and P bars respectively. Its slope is defined as the isokinetic (isoequilibrium) temperature, $\bar{\beta}$, which is independent of pressure. This equation is consistent with the B. S. El'yanov and E. M. Vasylvitskaya's result;[3]

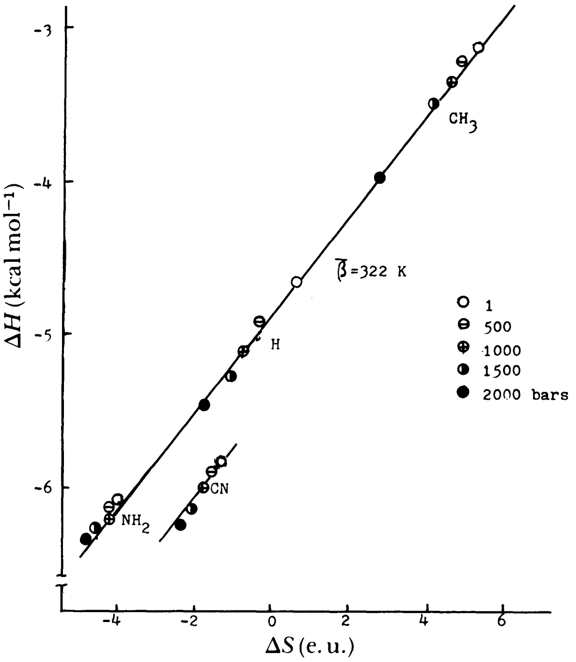


Fig. 1. The plot of ΔH vs. ΔS for changing pressure.

$$(\Delta H_P - \Delta H_0\ ) = (\Delta S_P - \Delta S_0) = -(n/m)(\Delta S_P - \Delta S_0), \qquad (13)$$

where m and n represent R ln $10(\partial V_0/\partial T)$ and R ln $10(\Delta V_0 - T\cdot\partial V_0/\partial T)$, respectively. The method of derivation in this paper is simpler than their method because this method derives the equation from the basic thermodynamic equation whereas their derivation required a complicated procedure by the use of a linear free energy relationship.[13]

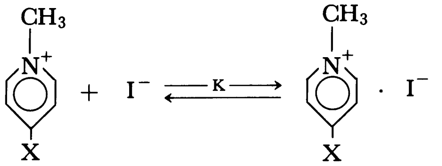
Similarly, integrating Eqs. 5 and 6, we have the following two equations;

$$(\Delta V_P - \Delta V_0) = \frac{\beta}{\alpha}(\Delta S_P - \Delta S_0) \qquad (14)$$

$$(\Delta H_P - \Delta H_0) = \frac{T\alpha - 1}{\beta}(\Delta V_P - \Delta V_0) \qquad (15)$$

From Eq. 12 and either one of these two equations, the values of α and β can be obtained.

Replacing Eq. 12, on the other hand, with the values of ΔH and ΔS listed in Table 2, we obtained the isoequilibrium relationship of the following reaction as shown Fig. 1.



The figure shows a satisfactory linearity as expected from Eq. 12. The slope, $\bar{\beta}$, is 322 K. The value of $\bar{\beta}$ deduced from Fig. 1 is independent of both substituent change and pressure change. It is very interesting and important for us to determine the mechanism of chemical reaction under high pressure. The $\bar{\beta}$ value is larger than the experimental temperature, 303.15 K, and hence the contribution to ΔG from ΔH is larger than that from ΔS. Accordingly, we could suggest the equilibrium of the above raction is enthalpy-controlled.

The present study was supported by the Basic Science Research Institute Program, Ministry of Education, Korea, 1985.

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