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Thermodynamic Properties of Caffeine in Compressed Gas

Jeong Rim Kim and Jin Burm Kyong

Department of Chemistry, Hanyang University, Ansan 425-791, Korea

Received February 4, 1995

The solubility of caffeine in compressed carbon dioxide has been measured to determine its fugacity coefficient between 330 and 410 K up to 500 bar. The result allows the calculation of the thermodynamic excess functions such as the molar excess enthalpy, the molar excess free energy, and the molar excess entropy. The pressure variations of the molar excess functions of caffeine in the caffeine-CO₂ mixture were discussed and also compared them with those in the caffeine-NH₃ mixture.

Introduction

The solubility of a solid in a gas at low pressure is given by the vapor pressure of the solid. According to the Raoult's law and the Dalton's law, the following relationship holds for the solid component in the gaseous phase at low pressure.

$$y_2 P = x_2 P_2^{\circ} \quad (1)$$

where y_2 is the mole fraction of the solid component in the gaseous phase, x_2 in the solid phase, and P is the total pressure of the gaseous phase and P_2° is the saturated vapor pressure of the solid component. Since we can assume that the mole fraction of gas in the solid phase is negligible at low pressure, the solubility of a solid in a gas is just the ratio of the vapor pressure to the total pressure. As the total pressure rises, equation (1) fails because of nonideal mixing in the gaseous phase which causes the fugacity of the solid component to be significantly different from its partial pressure. At higher pressures above the critical pressure of the gas, the nonideality of the gaseous phase becomes important in determining the solubility of the solid component.

There exist some partial data for the solubility of caffeine in carbon dioxide. They are the data up to 200 bar by Stahl and Schilz¹ and the data up to 160 bar by Ebeling and Franck.² There is also an equation for the solubility of caffeine in CO₂ in order to evaluate the interaction virial coefficients between caffeine and CO₂ by Lentz *et al.*³ This work reports the data on the solubility of caffeine in compressed carbon dioxide between 330 K and 410 K up to 500 bar and uses

them to determine the thermodynamic excess functions of caffeine due to mixing.

Thermodynamic Relationships

A binary system at temperature T and total pressure P consisting of caffeine as a heavy component 2 and carbon dioxide as a light component 1 will be considered in the present work. At equilibrium the distribution of the heavier component between the two phases of solid(S) and fluid(F) is governed by the Gibbs relation

$$f_2^S = f_2^F \quad (2)$$

The fugacity of caffeine (component 2) in the fluid phase is related to its mole fraction by

$$f_2^F = \phi_2 y_2 P \quad (3)$$

where ϕ_2 is the fugacity coefficient of caffeine in the fluid phase and y_2 is its mole fraction. On the other hand, if the mole fraction of a gas in a solid is negligible compared with unity, then the solid phase is considered to be pure and the fugacity of caffeine in the solid phase is given by

$$f_2^S = P_2^{\circ} \phi_2^{\circ} \exp \left[\int_{P_2^{\circ}}^P \frac{V_2^S}{RT} dP \right] \quad (4)$$

where ϕ_2° is the fugacity coefficient of the pure caffeine vapor and it is similar to unity because of the very low vapor pressure of pure caffeine. V_2^S is the molar volume of solid caffeine. Since we can assume V_2^S to be independent of pressure, equation (4) is rewritten

$$f_2^S = P_2^o \exp\left[\frac{V_2^S}{RT} P\right] \quad (5)$$

When equations (3) and (5) is substituted into equation (2), the logarithmic fugacity coefficient of caffeine in the fluid phase is

$$\ln \phi_2 = -\frac{V_2^S}{RT} P - \ln\left(y_2 \frac{P}{P^o}\right) \quad (6)$$

The values of the logarithmic fugacity coefficients at several temperatures allow us to compute the thermodynamic excess functions such as the molar excess enthalpy (H^E), the molar excess free energy (G^E), and the molar excess entropy (S^E) due to mixing. When solid caffeine is dissolved in compressed carbon dioxide, the molar excess functions of caffeine due to mixing are given by

$$H_2^E = R \left[\frac{\partial \ln \phi_2}{\partial (1/T)} \right]_P, \quad (7)$$

$$G_2^E = RT \ln \phi_2, \quad (8)$$

$$S_2^E = \frac{H_2^E - G_2^E}{T}. \quad (9)$$

Experimental

Anhydrous caffeine of purity >99% (Fluka AG, Switzerland) and carbon dioxide of purity >99% (Daesung OX. Co. Korea) were used without further purification. The equipment used is given elsewhere⁴ and was similar in principle to the dynamic method used for the solubility measurements in carbon dioxide³ and in ammonia.⁵ Carbon dioxide was compressed by a metering pump (NOVA, Switzerland) and passed through a heat exchanger to an autoclave which plays a role as the equilibrium cell. The dimension of this autoclave was 2.0 cm of inner diameter, 2.8 cm of outer diameter, and 50.0 cm of height. To accomplish the equilibrium the autoclave was filled with small rolls of glass wool and caffeine. The height of this packing was about 40 cm since at both ends 5 cm were occupied by stoppers with glass wool.

The loaded carbon dioxide was expanded by a valve into a weighed glass vessel in order to obtain the precipitated caffeine. The solubility y_2 could be determined from the amounts of the precipitated caffeine and the expanded carbon dioxide. The time for a measurement has to be substantial and the amount of carbon dioxide used has to be large if the solubility is small. Hence, for a practical convenience and also because of decreasing precision, the lower limit of solubilities in the method employed was 1×10^{-6} mole fraction. The temperature and the pressure of measuring the solubility were also limited because of the increasing danger due to the heating of the tubes and the autoclave under the elevated pressure.

The autoclave was positioned vertically. A horizontal position led to remarkably higher values of the solute concentrations, probably due to mechanical transport of small caffeine particles or of parts of a caffeine-rich phase.

The pressures were measured within ± 2 bar by a Bourdon gauge at the expansion valve and at the pump, simultaneously. The temperature was raised by the resistance heat-

Table 1. Data of Solubilities and Fugacity Coefficients of Caffeine in Carbon Dioxide at Several Temperatures and Pressures

T (K)	P (bar)	y_{caff} (10^{-4})	$\ln E^*$	$\ln \phi_{caff}$	P_{caff}^o (bar)
330	100	0.016	8.5260	-8.0369	3.172×10^{-8}
	200	0.540	12.7382	-11.7600	
	300	0.590	13.2321	-11.7647	
	400	0.560	13.4677	-11.5112	
	500	0.530	13.6358	-11.1902	
370	100	0.052	5.5086	-5.0724	2.107×10^{-6}
	200	1.150	9.2981	-8.4256	
	300	2.934	10.6402	-9.3315	
	400	3.676	11.1532	-9.4082	
	500	4.581	11.5964	-9.4152	
410	100	0.163	3.2630	-2.8693	6.238×10^{-5}
	200	2.180	6.5495	-5.7621	
	300	10.114	8.4896	-7.3086	
	400	15.735	9.2193	-7.6446	
	500	26.564	9.9660	-7.9976	

E^* indicate $y_{caff} \frac{P}{P_{caff}^o}$ which is called the enhancement factor.

ers and kept constant within ± 0.2 °C by an electric thermostat. Temperature were measured by chromel-alumel thermocouples. For temperature regulation these thermocouples were placed outside of the wall of the autoclave and heat exchanger, respectively.

The reproducibility of the measurement was within 10^{-5} in this work.

Results and Discussion

The original values of measured solubilities of caffeine in carbon dioxide as a function of temperature and pressure are given in the third column of Table 1. Figure 1 shows the isobaric and isothermal solubility of caffeine in compressed carbon dioxide as a function of the CO₂ density evaluated from the P - V - T data⁶ of carbon dioxide. The measured points are indicated by circles in Figure 1 and seem to agree with the data reported by Lentz *et al.*³

The vapor pressure of pure caffeine P_{caff}^o in Table 1 is calculated by the relation given by Ebeling and Franck.²

$$\log P_{caff}^o = 7.46 - \frac{5411}{T} + \log(0.08314T).$$

The second term in the right hand side of equation (6) can be calculated from the experimental solubility and is shown in the fourth column of Table 1. In order to obtain the first term in the right hand side of equation (6), $\bar{V}_{caff}^o = 134.2$ cm³·mol⁻¹ was taken from the literature.⁷ The logarithmic fugacity coefficients as the resultant values of two terms of equation (6) are also listed in Table 1. The complete collinearities were obtained by isobaric plots of the logarithmic fugacity coefficient against reciprocal temperature as shown in Figure 2, resulting in the molar excess enthalpies of caffeine due to mixing into compressed carbon dioxide.

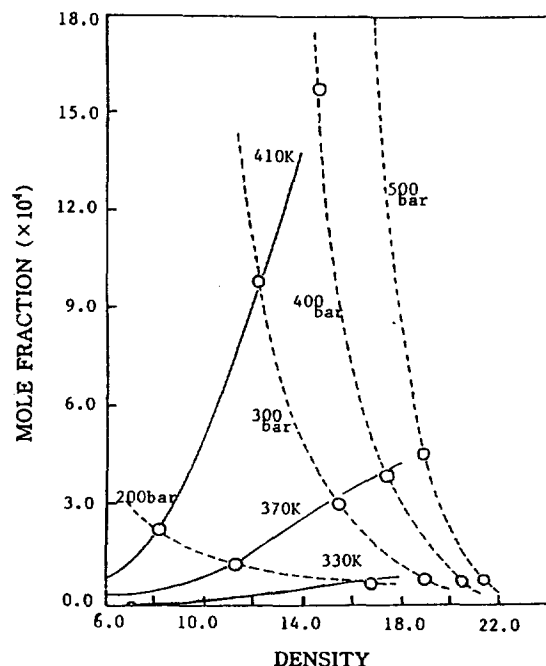


Figure 1. Mole fractions of caffeine in compressed CO₂ as a function of CO₂ density. The experimental points (circles) are indicated as isobars by dashed curves and the solid curves are isotherms reported by Lentz *et al.*

Table 2. Thermodynamic Excess Functions of Caffeine in Carbon Dioxide

P (bar)	T (K)	H_{caff}^E (kJ/mol)	G_{caff}^E (kJ/mol)	S_{caff}^E (J/mol·deg)
100	330		-22.050	-153.93
	370	-72.847	-15.604	-154.71
	410		-9.781	-153.82
				(av. -154.15)
200	330		-32.265	-158.08
	370	-84.431	-25.919	-158.14
	410		-19.642	-158.02
				(av. -158.08)
300	330		-32.278	-92.13
	370	-62.681	-28.705	-91.83
	410		-24.913	-92.12
				(av. -92.03)
400	330		-31.582	-69.08
	370	-54.379	-28.941	-68.75
	410		-26.058	-69.08
				(av. -68.97)
500	330		-30.702	-43.15
	370	-44.943	-28.963	-43.19
	410		-27.262	-43.12
				(av. -43.15)

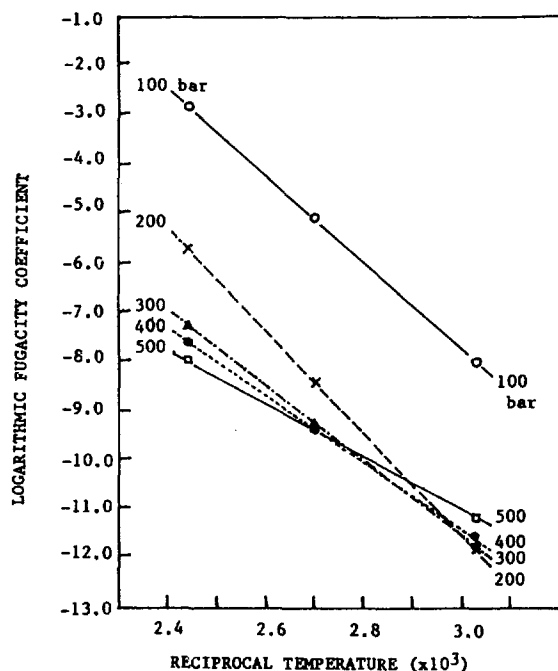


Figure 2. Isobaric plots of the logarithmic fugacity coefficient of caffeine in compressed CO₂ against the reciprocal temperature at various pressures.

On the other hand, the logarithmic fugacity coefficient permits us to evaluate the molar excess free energy at desired temperature and pressure by equation (8). When once the molar excess enthalpy and free energy are obtained, it is possible to determine the isobaric molar excess entropy ac-

ording to equation (9). The three thermodynamic quantities at several pressures and temperatures are given in Table 2 for caffeine of dissolving in carbon dioxide. For clearness of the variation with pressure, the obtained molar excess quantities H^E , G^E , and TS^E at 330 K and 410 K are plotted against pressure in Figure 3. For caffeine dissolved in carbon dioxide the molar excess enthalpy and the molar excess entropy decrease as the pressure elevates up to about 150 bar. In the same region the molar excess free energy decreases only slightly.

The molar excess enthalpy and the molar excess entropy change to smaller negative values at higher pressure than 150 bar as the pressure elevates. Furthermore, they change more slightly above 300 bar as the pressure elevates. The isobaric excess enthalpy in this work is an isobaric transition energy of caffeine from its pure gas at P_{caff}^0 to the caffeine-CO₂ mixture with caffeine content y_{caff} at total pressure P . The isobaric transition energy of caffeine into carbon dioxide has highest value of nearly $-90 \text{ kJ}\cdot\text{mol}^{-1}$ at about 150 bar. In Figure 3, its negative value decreases at higher pressure than 150 bar as the pressure elevates. Therefore, we can expect that the isobaric transition energy of caffeine into carbon dioxide has a small negative value to be constant at extremely high pressure. The decrease in the isobaric excess entropy at lower pressure than 150 bar can be explained by the effect of pressure on the free volume of the compressed gas but the decrease in the nonideal entropy of mixing at higher pressure than 150 bar in Figure 3 reflects a smaller randomness of the system at high pressure. The variation of the isobaric excess entropy of caffeine in carbon dioxide with pressure shows the similar fashion to the case

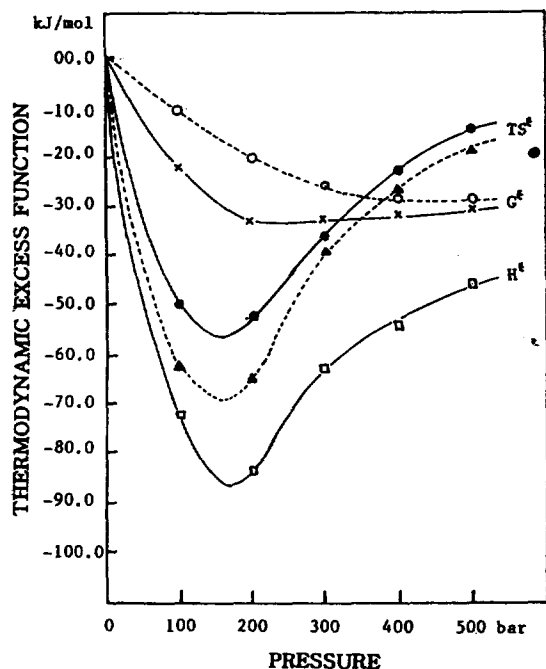


Figure 3. Variations of thermodynamic excess functions of caffeine in compressed CO_2 with pressure at 330 K (solid curves) and 410 K (dashed curves)

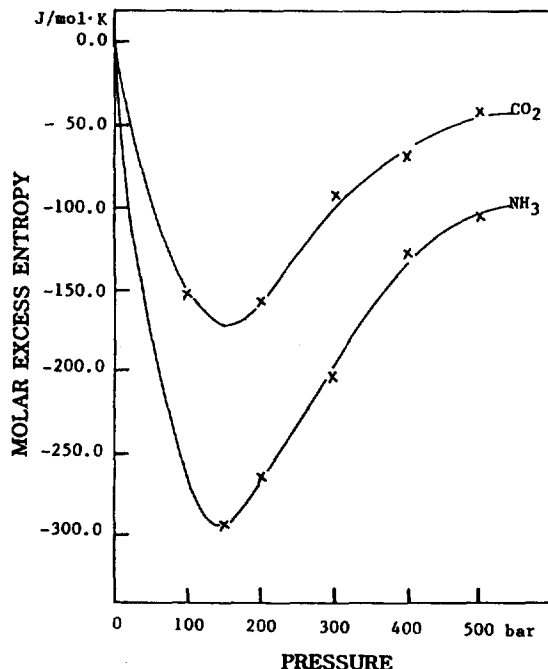


Figure 5. Pressure variations of the molar excess entropies of caffeine in carbon dioxide and in ammonia.

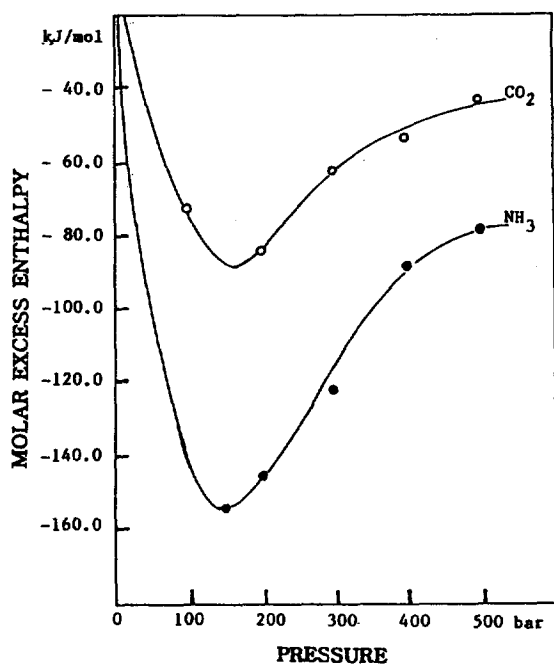


Figure 4. Pressure variations of the molar excess enthalpies of caffeine in carbon dioxide and in ammonia.

of its enthalpy.

As shown in Figure 3, the molar excess free energy decreases slightly at 410 K as the pressure elevates while that at 330 K increases very slightly with pressure after the relatively larger decrease than at 410 K in the region of pressure below about 300 bar. The excess free energy is a measure of the transference of caffeine to carbon dioxide

at desired temperature and pressure. At 330 K, the transference of caffeine to carbon dioxide is largest when the pressure is about 300 bar and it is in complete agreement with the solubility data. The pressure at which the maximum transference appears elevates with the temperature rising.

In the present study, it can be seen that the transference of caffeine to carbon dioxide is governed by the excess entropy at the pressure below 300 bar and by the excess enthalpy at the pressure above 400 bar.

On the other hand, it was compared the molar excess enthalpies and entropies of caffeine between the cases in carbon dioxide and in ammonia, although those of caffeine in ammonia were evaluated from the previous paper.⁵ The molar excess enthalpy of caffeine in compressed carbon dioxide is always larger than that in compressed ammonia, and the variations of both cases with pressure show a similar fashion, as shown in Figure 4. Since the negative values of the molar excess enthalpies of caffeine in ammonia were obtained to be more than 1.7 times of those in carbon dioxide at various pressures, it is seemed that the transition of caffeine into ammonia is more favourable than that into carbon dioxide provided that the all conditions are same. Similarly, the molar excess entropy of caffeine in compressed ammonia is also less than that in compressed carbon dioxide as shown in Figure 5. These behaviors may be attributed to the increase in the solubility of caffeine in ammonia because of a high basicity for ammonia as compared to carbon dioxide.

The ionization constants for caffeine, carbon dioxide, and ammonia are $K_a(\text{H}_2\text{O}) < 1.0 \times 10^{-14}$ at 25 °C,⁸ $K_a(\text{H}_2\text{O}) = 5.61 \times 10^{-11}$ at 25 °C,⁹ and $K_a(\text{H}_2\text{O}) = 5.64 \times 10^{-10}$ at 25 °C,⁹ respectively. Thus, it can be expected that in the non-aqueous environment of caffeine, ammonia should strongly interact with caffeine due to its progressed ionization.¹⁰ This could lead to a pronounced solvent-solute interaction between ammonia

and caffeine.

Acknowledgment. This work was financially supported by the research fund from Hanyang University, 1993

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Rotational State Distribution of NO after Collisions with Fast Hydrogen Atom

Yoo Hang Kim and David A. Micha[†]

Department of Chemistry, Inha University, Incheon 402-751, Korea

[†]*Departments of Chemistry and of Physics, University of Florida, Gainesville, Florida 32611, U. S. A.*

Received February 4, 1995

Based on the collisional time-correlation function approach a general analytical expression has been derived for the double differential cross-section with respect to the scattering angle and the final rotational energy, which can be applied to molecules with non-zero electronic orbital angular momentum after collision with fast hydrogen atoms. By integrating this expression another very simple expression, which gives the final rotational distribution as a function of the rotational quantum number, has also been derived. When this expression is applied to $\text{NO}({}^2\Pi_{1/2}, v'=1)$ and $\text{NO}({}^2\Pi_{3/2}, v'=1, 2, 3)$, it can reproduce the experimental rotational distribution after collision with fast H atom very well. The average rotational quantum number and average rotational energy calculated using this expression are also in good agreement with those deduced from the experimental distributions.

Introduction

Several years ago we derived an expression for the double differential cross section (with respect to scattering angles and final rotational energies) of molecules with a thermal distribution of initial rotational states colliding with fast atoms.¹ This expression, based on the collisional time-correlation function formalism, is valid when the collision time is short compared with the periods of internal motions of target molecules.

The formulation gave a simple final rotational distribution in terms of the error function, which can be used to parametrize experimental results. The derived expression was applied to the experimentally measured final rotational distributions of \sum electronic state molecules CO and CO₂ colliding with fast hydrogen atoms,^{2,3} for which the total electronic angular momentum is zero. It was found that for CO($v'=1$) and CO₂(00⁰1), in which the collisions are impulsive, the derived formula fitted the experimental results very well. For CO($v'=0$), in which long-duration, complex-forming collisions play an important role, however, an additional statistical distribution as suggested by surprisal analysis⁴ was necessary

to explain the experimental distribution satisfactorily.

There have been continued interests in the collisional energy transfer between fast, mono-energetic hydrogen atom (H or D) and simple diatomic or triatomic molecules such as CO,^{5,6} NO,⁷ H₂O⁸ and CO₂.⁹⁻¹³

In this work we have extended our theory and obtained a modified expression which can be applied to molecules with non-zero total electronic angular momentum and report the result for H+NO(${}^2\Pi_{1/2}$, ${}^2\Pi_{3/2}$) collision systems.

Formulation

The rotational energy for Hund's case (a) molecules, neglecting centrifugal distortion terms, can be expressed as¹⁴

$$E_r = Bhc [J(J+1) - \Omega_e^2], \quad J \geq \Omega_e \quad (1)$$

where Ω_e is the component of the total electronic angular momentum along the internuclear axis and B is the rotational constant; h and c have their usual meanings.

With this expression replacing Eq. (14.e) in Reference 1 and all the E_r terms therein, the remaining derivation follows