The Vacancies–in–Solid Model Applied to Sublimation Pressure, Enthalpies and Entropies of Sublimation, and Enthalpies and Entropies of Solid Krypton and Xenon

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Thermodynamic properties such as sublimation pressures, enthalpies and entropies of sublimation, enthalpies and entropies of solid krypton and xenon are calculated from $0\,°K$ to the triple point, using the vacancies–in–solid model. The Mie–Lennard–Jones 12,6 potential in uniform potential field is used. The results are compared with the calorimetric and sublimation pressure values, and are in a good agreement with the available calorimetric and sublimation pressure values.

Introduction

During the past, thermodynamic properties of the rare gas solids have theoretically created much interest because their atoms are characterized by the tightly bound, closed-shell structure, spherical symmetry, and weak interatomic force, and interatomic forces between their atoms are relatively accurately described. Highly accurate data of thermodynamic properties for the solids are necessary because they can be compared with theoretical predictions based on proposed models. Sublimation pressures of solid krypton and xenon have been measured by some investigators over past scores of years. Chen *et al.*[1,2] have measured sublimation pressures of solid argon, krypton and xenon, and obtained their semi-empirical enthalpies of sublimation which were derived from their sublimation pressure measurements via the Clausius-Clapeyron equation. Schwalbe *et al.*[3] have determined the calorimetric enthalpy and entropy of solid argon, krypton and xenon by the following thermodynamic relationships.

$$H_{cal}(T,P)=H_R+\int_{T_R}^{T}C_{sat}dT+\int_{P_R}^{P}VdP \tag{1}$$

$$S_{cal}(T,P)=\int_{0}^{T}(C_{sat.}/T)dT \tag{2}$$

where C_{sat} is the saturated heat capacity of the condensed phase along the saturated sublimation pressure curve, and V the molar volume of the condensed phase at arbitrary point (T, P). H_R denotes the enthalpy at some reference temperature T_R.

Although there have been numerous experimental studies of solid krypton and xenon, few theories can explain their thermodynamic properties quantitatively from $0\,°K$ up to the triple point. In previous papers,[4-6] we have derived a solid partition function for monatomic crystals on the basis of the vacancies-in-solid model which have taked account of lattice vacancy defects and two maximum phonon frequencies for perfect crystals, and used the modified Mie-Lennard-Jones 12,6 potential. We have also studied the sublimation pressures of solid argon and xenon, and molar volumes and isothermal compressibilities of solid krypton and xenon. In this paper, we have used the same vacancies-in-solid model and evaluated sublimation pressures, enthalpies and entropies of sublimation, and ehthalpies and entropies of solid krypton and xenon from $0\,°K$ to the triple point. And also, we have compared our results with observed data, available calorimetric data and semi-empirical values derived from sublimation pressures. Finally, we are to test for availability of our vacancies-in-solid model.

The Partition Function

According to the vacancies-in-solid model,[4-6] the canonical ensemble partition function $Q(N, x, T)$ for monatomic crystals is written as

$$Q(N,x,T)=\frac{(N+N_h)!}{N!N_h!}q_c^{xN}(q_\alpha+q_\beta)^{(1-x)N}$$

$$=\frac{(N+N_h)!}{N!N_h!}q_c^{N}(1+\Delta)^{(1-x)N} \tag{3}$$

where

$$q_c=q_\alpha=\left(2\sinh\frac{\theta_c}{2T}\cdot 2\sinh\frac{\theta_D}{2T}\right)^{-3/2}e^{-\phi c/kT},$$

$$q_\beta=q_n=\left(2\sin h\frac{\theta_c}{2T}\right)^{-3}e^{-\phi_\beta/kT},$$

$$x=V_0/V=(a_0/a)^3$$

$$\Delta=q_\beta/q_\alpha$$

and

$$-\Phi_c(x)=-N\phi_c(x)=U_e+D_e(2x^2-x^4).$$

Here q_c, q_α and q_β represent the molecular partition functions of the perfect oscillator of the perfect crystal-like part, the imperfect oscillator of the imperfect crystal-like part in α-state and β-state, respectively. θ_D is the Debye temperature, and θ_c is given in order to $(4/7)\,\theta_D\cdot\phi_c$ and ϕ_β are the

static potential energy of a perfect oscillator and an imperfect oscillator in β-state, respectively. x is a probability of finding atoms at the first neighboring lattice sites. U_e is the minimum potential energy per mole in the uniform potential field. D_e is the dissociation energy per mole required to separate stable atomic pairs far apart to infinitive distance in the uniform potential field. N and N_h are the number of atoms and lattice vacancies in crystals, respectively. E_0 is the difference between the static potential energy per mole of the perfect oscillator and the imperfect oscillator in β-state. V_0 and V are the molar volume at $0\,°K$ and at a given temperature, respectively. The parameters E_0, U_e and D_e have been determined by Ko *et al.* and suggested in the previous paper.[6] Calculations were made on the Hewlett Packard 3000–series 2 computer.

Results

Utilizing the condition that the Gibbs free energy for a solid is equal to that of a vapor, the following equation of the sublimation pressure is obtained from the above solid partition function, using the virial equation of state.

$$\ln(P/\text{atm}) = j^G + \left(\frac{5}{2}\right)\ln T + \left(\frac{3}{2}\right)\ln 2\sinh\frac{\theta_c}{2T}$$
$$\cdot 2\sin h\frac{\theta_D}{2T} - \frac{D}{RT} + (2x-1)\ln(1+\Delta) + \ln(x) - \ln(1-x) \quad (4)$$

where

$$D = [U_e + D_e(6x^2 - 5x^4)] + (1/2)(PB_v)^2/RT] \quad (4a)$$

and;

$$j^G = \ln\left(\frac{2\pi mk}{h^2}\right)^{3/2}(k/1.01325\times10^6)$$

where B_v is the second volume virial coefficient of the vapor. j^G are 2.9777 and 3.6507 for krypton and xenon, respectively. The potential parameter U_e is determined by solving the equation of the sublimation pressure (4), using observed triple point properties, *i.e.* the triple point temperature, the sublimation pressure and the molar volume at the triple point, and the molar volume at $0\,°K$. U_e is dependent upon whether a gas imperfection is considered or not. The second virial coefficient represents the effect of the gas imperfection in the vapor phase upon the sublimation pressure. For the solid krypton and xenon the effect of the gaseous imperfection on U_e is only 0.08 cal/mole, and decreases the magnitude of U_e. If we consider a significant figure, the gaseous imperfection seems hardly to influence the value of U_e. Since effects of the third virial coefficients on U_e are by far smaller than the second virial coefficients, moreover contributions from third and higher order virial coefficiedts may be ignored. As mentioned in the coming discussions, the gaseous imperfection has a very small effect on the sublimation pressure and enthalpies and entropies of sublim ation. In the case of the ideal gas which has neglected the gaseous imperfection, the calculated results of sublimation pressures for solid krypton are presented in Table 1 along with recent observed data for comparison,

TABLE 1: Sublimation Pressures of Solid Krypton

$T(°K)$	Theory(torr)	Obs(torr)[a]	Obs(torr)[b]	Obs(torr)[c]	Obs(torr)[d]
115.763	547.5	547.2	545.7	547.1	546.9
115	507.1	507.0	505.6	507.1	506.6
114	458.1	458.1	456.8	458.4	457.6
112	371.5	371.9	370.8	372.5	371.3
110	298.8	299.6	298.7	300.4	298.9
108	238.4	239.5	238.7	240.4	238.8
106	188.6	189.8	189.2	190.7	189.1
104	147.7	149.1	148.6	150.0	148.5
102	114.7		115.6	116.8	115.4
100	88.0		89.0	90.1	88.9
95	43.2		44.2	44.9	44.0
90	19.6		20.3	20.7	20.2
85	8.1		8.3	8.7	
80	3 0				
75	1.0				
70	0.3				
65	6.0×10^{-2}				
60	1.0×10^{-2}				

[a]Ref. 1, [b]ref. 2, [c]ref. 7, [d]ref. 8.

TABLE 2: Sublimation Pressure of Solid Xenon

$T(°K)$	Theory(torr)	Obs(torr)[a]	Obs(torr)[b]	Obs(torr)[c]	Obs(torr)[d]
161.39	612.4	612.3	613.8		
160	553.9	554.1	555.4	553	
158	478.2	478.6	479.5	478.1	
156	411.1	411.7	412.4	411.8	
154	352.1	352.8	353.3	353.3	
152	300.3	301.2	301.5	301.9	
150	254.9	256.0	256.1	256.9	
145	165.9	167.1	167.1	168.3	
140	104.5		105.8	107.0	
135	63.6		64.7	65.7	
130	37.2		38.1	38.9	
125	20.8		21.5	22.1	
130	37.2		38.1	38.9	
125	20.8		21.5	22.1	
120	11.1		11.6	12.0	
115	5.6		5.9	6.1	
110	2.6		2.8	3.0	2.9
100	4.7×10^{-1}				5.1×10^{-1}
90	5.6×10^{-2}				6.1×10^{-2}
80	3.9×10^{-3}				4.2×10^{-3}
70	1.3×10^{-4}				1.4×10^{-4}

[a]Ref. 1, [b]ref. 2, [c]ref. 8, [d]ref. 17.

and for solid xenon, in Table 2. The observed subilmation pressures for solid krypton and xenon are taken from Chen *et al.*[1], Leming *et al.*[2] Beaumont *et al.*[7] and Freeman *et al.*[8] As shown in Table 1 and 2, the calculated results of sublimation pressures for solid krypton and xenon are in a good agreement with observed data within an experimental error, although the gaseous imperfection has been neglected.

The expressions for enthalpies and entropies of sublimation of the solid are also written as follows.

$$\Delta H = \left(\frac{5}{2}\right)RT + [U_e + D_e(6x^2 - 5x^4)] + PB_v(T)$$

TABLE 3: Enthalpies and Entropies of Sublimation, Enthalpies and Entropies of Solid Krypton

| T(°K) | ΔH (J/mole) | | ΔS (J/mole-°K) | H (J/mole) | | S(J/mole-°K) | |
	Semi–Empirical[a]	Calculated[b]	Calculated	Calorimetric[c]	Calculated	Calorimetric[d]	Calculated
115	10773+17	11108	96.59		8718		50.94
		(11085)[f]	(96.57)				
114.853		11109	96.73	−8489+15	−8720	52.98+0.26	50.91
114	10797+16	11115	97.50		−8746		50.70
		(11094)[f]	(97.48)				
113	10819±16	11123	98.43		−8774		50.45
112.642		11126	98.77	−8567	−8782	52.29	50.36
112	10840±15	11130	99.38	—	−8802		50.20
		(11112)[f]	(99.36)				
111.612		11133	99.75	−8603	−8811	51.97	50.10
111	10860±15	11137	100.34		−8830		49.95
	10929[e]						
110	10879±14	11145	101.32		−8858		49.69
		(11129)[f]	(101.30)				
109.879		11145	101.43	−8664	−8859	51.43	49.66
109	10896±14	11152	102.31		−8806		49.44
108.506		11155	102.81	−8710	−8898	51.00	49.31
108	10913±14	11159	103.32		−8914		49 18
		(11147)[f]	(103.31)				
107.743		11161	103.58	−8736±16	−8919	50.77±0.25	49.12
106.831		11167	104.53	−8766	−8944	5048	48.88
106	10943±14	11173	105.40		−8970		48.66
105.827		11174	105.59	−8800	−8972	5017	48.62
105.475		11177	105.96	−8812	−8982	50.06	48 52
104.794		11181	106.70	−8834	−9001	49.85	48.34
104	1070±15	11187	107.57		−9026		48.13
102.8	11029[e]	11195	108.90		−9056		47 81
102	10993±17	11201	109.81		−9081		−47.60
100		11215	112.15		−9136		−47.05
94.3	11171[e]	11252	119.32		−9290		−45.44
90		11280	125.33		−9409		−44 17
82	11063[e]	11329	138.16		−9625		−41.66
80		11341	141.76		−9678		41.00
70		11397	162.81		−9942		37.48
63.2	11632[e]	11431	180.88		−10116		34.84
60		11446	190.77		−10199		33.51
50		11489	229.78		−10450		28.95
40		11520	288.00		−10688		23.62
30		11533	384.45		−10910		17.28
20		11512	575.61		−11096		9.77
10		11419	1141.9		−11211		2.23

[a]Derived from sublimation pressures *via* the Clausius–Clapeyron equation by Chen *et al.*[1](1978); [b]Calculated from eq. 5 by neglecting gaseous imperfection term; [c]Calculated from eq. (1) by Schwalbe *et al.*[3] (1977); [d]Calculated from eq. (2) by Schwalbe *et al.*[3] (1977); [e]Derived from sublimation pressures *via* the Clausius–Clapeyron equation by Leming *et al.*[2] (1—70); [f]Calculated from eq. 5 by considering gaseous imperfection term.

$$-\frac{3}{2}RT\left(\frac{\theta_c}{2T}\coth\frac{\theta_c}{2T}+\frac{\theta_D}{2T}\coth\frac{\theta_D}{2T}\right)-(1-x)\left(\frac{\Delta}{1+\Delta}\right)$$

$$\cdot RT\left[\frac{3}{2}\left(\frac{\theta_c}{2T}\coth\frac{\theta_c}{2T}-\frac{\theta_D}{2T}\coth\frac{\theta_D}{2T}\right)+E_0/kT\right]$$

$$+xRT\ln(1+\Delta)+\frac{RT}{x}\ln(1-x) \tag{5}$$

$$\Delta S/R=2.5+\frac{U_e+D_e(6x^2-5x^4)}{RT}-\frac{1}{x}\ln(1+\Delta)$$

$$+\frac{1}{x}\ln(1-x)-\frac{3}{2}\left(\frac{\theta_D}{2T}\coth\frac{\theta_D}{2T}+\frac{\theta_c}{2T}\coth\frac{\theta_c}{2T}\right)$$

$$-(1-x)\left(\frac{\Delta}{1+\Delta}\right)\left[\frac{3}{2}\left(\frac{\theta_c}{2T}\coth\frac{\theta_c}{2T}-\frac{\theta_D}{2T}\coth\frac{\theta_D}{2T}\right)\right.$$

$$\left.+E_0/RT\right]+\frac{PB_v(T)}{RT} \tag{6}$$

In the case of the ideal gas, the results of enthalpies and entropies of sublimation for solid krypton and xenon calculated by eqs. (5) and (6) are, respectively, presented in Table 3 and 4 along with recent semi-empirical enthalpies of sublimation. Enthalpies and entropies of sublimation at the triple point are specially presented in Table 5. As

TABLE 4: Enthalpies and Entropies of Sublimation, Enthalpies and Entropies of Solid Xenon

| T(°K) | ΔH (J/mole) | | ΔS (J/mole-°K) | H (J/mole) | | S (J/mole-°K) | |
	Semi–Empirical[a]	Calculated[b]	Calculated	Calorimetric[c]	Calculated	Calorimetric[d]	Calculated
161	14999±48	15441	95.91		−12095		62.88
160.563		15445	96.19	−11820±20	−12106	64.72±0.32	62.81
160	15020±45	15449 (15420)[f]	96.56		−12123		62.71
159.766		15451	96.71	−11852	−12128	64.55	62.66
159	15041±43	15457	97.21		−12152		62.53
158.118		15463	97.80	−11916±21	−12175	64.18	62.37
158	15061±41	15464 (15439)[f]	97.88		−12180		62.35
157	15080±39	15742	98.55		−12209		61.17
156	15098±37	15804 (15458)[f]	99.23		−12237		61.98
156.1	14560[e]	15479	99.16		−12232		62.00
155.359		15485	99.67	−120192	−12254	63.56	61.87
155	15115±35	15487	99.92		−12267		61.80
154	15131±34	15495 (15476)[f]	100.62		−12294		61.62
153.882		15496	100.70	−12070	−12296	63.22±0.32	61.60
153	15146±32	15502	101.32		−12322		61.43
152	15161±31	15510 (15493)[f]	102.04		−12351		61.25
151.467		15514	102.43	−12154±22	−12364	62.68±0.31	61.15
151	15175±30	15518	102.77		−12379		61.04
150	15188±29	15525 (15510)[f]	103.50		−124 7		60.87
149.189		15531	104.11	−12231	−12429	62.17	60.72
149	15200±28	15533	104.25		−12436		60.68
148	15212±28	15540	105.00		−12464		60.49
147	15223±27	15548	105.77		−12492		60.30
146.636		15550	106.05	−12316±23	−12501	61.59	60.23
146	15234±27	15555	106.54		−12520		60.11
145	15243±26	15562	107.33		−12548		59.92
144.814		15564	107.47	−12376	−12552	61.18	59.88
144.6	15046[e]	15565	107.65		−12559		59.84
144	15253±26	15570	108.12		−12577		59.72
143	15261±26	15577	108.93		−12605		59.52
140		15599	111.42		−12689		58.93
133	15318[e]	15649	117.66		−12884		57.50
130		15670	120.54		−12967		56.86
115.5	15196[e]	15767	136.51		−13366		53.61
100		15866	158.66		−13787		49.70
90.1	16297[e]	15925	176.74		−14050		46.91
80		15981	199.77		−14319		43.77
60		16082	268.03		−14835		36.36
40		16156	403.90		−15324		26.45
20		16165	808.27		−15750		11.96
10		19091	1609.11		−15883		3.10

[a]Derived from sublimation pressures *via* the Clausius-Clapeyron equation by Chen *et al.*[1] (1978); [b]Calculated from eq. 5 by neglecting gaseous imperfection term; [c]Calculated from eq. (1) by Schwalbe *et al.*[3] (1977); [d]Calculated from eq. (2) by Schwalbe *et al.*[3] (1977); [e]Derived from sublimation pressures *via* the Clausius–Clapeyron equation by Leming *et al.*[2] (1970); [f]Calculated From eq. 5 by considering gaseous imperfection term.

shown in Tables 3, 4 and 5, the maximum errors of semi-empirical enthalpies and entropies of sublimation for solid krypton and xenon emerge at triple point, and for krypton are about ±0.16 percent and ±0.29 percent, respectively,

and for solid xenon, about ±0.33 percent and ±0.45 percent. Although the gaseous imperfection is neglected, all calculated enthalpies of sublimation for solid krypton and xenon are somewhat larger than Chen's *et al.* semi-empirical

TABLE 5: Triple Point Properties of Solid Krypton and Xenon

	Krypton		Xenon	
	Calc.	Obs.	Calc.	Obs.
Gas enthalpy	2406[e]	2334±7[b]	3355[e]	3254±10[b]
	2384[f]		3324[f]	
Gas entropy	147.04[e]	146.67±0.08[a]	158.61[e]	158.31±0.08[a]
	146.83[f]		158.42[f]	
Solid enthalpy	−8694	−8457±15[b]	−12082	−11785±20[b]
Solid edtropy	51.13	53.46±0.25[a]	62.95	65.19±0.42[a]
		53.26±0.27[b]		64.91±0.32[b]
Enthalpy of sublimation	11102[e]	10792±25[a]	15438[e]	15041±83[a]
		10784±58[a]		15033±38[a]
		10791±13[b]		15039±22[b]
	11078[f]	10754±17[g]	15407[f]	14990±49
Entropy of sublimation	95.91[e]	93.22±0.11[b]	95.66[e]	93.12[c]±0.42
	95.70[f]	93.21±0.25[c]	95.47[f]	93.40±0.32
		93.41±0.27[d]		

Enthalpies and entropies are given in units of J/mole and J/mole-°K, respectively.

[a]Ref. 14, p. 672 and 689; [b]Ref. 3; [c]Calculated using the triple point entropy of the solid and the gas in ref. 1; [d]Calculated using ref. 14 data as the triple point entropy of the gas and ref. 3 data as the triple point entropy of the solid; [e]Calculated taking no account of gaseous imperfection; [f]Calculated taking account of gaseous imperfection; [g]ref. 1.

enthalpies of sublimation[1]. Maximum relative differences between calculated and semi-empirical values of enthalpies and entropies of sublimation emerge at triple point. Although these are dependent upon semi-empirical values, these differences are about 2.6 percent. The realtive differences are somewhat large than errors which Chen et al.[1-3] have mentioned, but decrease with decreasing temperatures.

The expressions for the solid enthalpy and the solid entropy are derived from the solid partition function as follows.

$$H = \frac{3}{2}RT\left(\frac{\theta_D}{2T}\coth\frac{\theta_D}{2T} + \frac{\theta_c}{2T}\coth\frac{\theta_c}{2T}\right)$$

$$-[U_e + D_e(6x^2 - 5x^4)] + (1-x)\left(\frac{\Delta}{1+\Delta}\right)$$

$$\left[\frac{3}{2}RT\left(\frac{\theta_c}{2T}\coth\frac{\theta_c}{2T} - \frac{\theta_D}{2T}\coth\frac{\theta_D}{2T}\right) + E_0\right]$$

$$+ xRT\ln(1+\Delta) - \frac{RT}{x}\ln(1-x) \qquad (7)$$

$$S/R = -\ln x - \left(\frac{1-x}{x}\right)\ln(1-x) - \frac{3}{2}\ln\left(2\sinh\frac{\theta_c}{2T}\right.$$

$$\left.\cdot 2\sinh\frac{\theta_D}{2T}\right) - (1-x)\ln(1+\Delta) + \frac{3}{2}\left(\frac{\theta_c}{2T}\coth\frac{\theta_c}{2T}\right.$$

$$\left.+ \frac{\theta_D}{2T}\coth\frac{\theta_D}{2T}\right) + (1-x)\left(\frac{\Delta}{1+\Delta}\right)\left[\frac{3}{2}\left(\frac{\theta_c}{2T}\coth\frac{\theta_c}{2T}\right.\right.$$

$$\left.\left.- \frac{\theta_D}{2T}\coth\frac{\theta_D}{2T}\right) + E_0/RT\right] \qquad (8)$$

Using eqs. (7) and (8), the calculated results of the solid enthalpy and the solid entropy for krypton and xenon are, respectively, presented in Table 3 and 4 along with Schwalbe's et al. recent calorimetric enthalpies and entropies. As shown in Tables 3, 4 and 5, the errors of calorimetric enthalpies and entropies are about ± 0.18 percent and ±0.50 percent, respectively. All calculated solid enthalpies and entropies for krypton and xenon are somewhat smaller than the calorimetric solid enthalpies and entropies which Schwalbe et al.[3] have calculated by eqs. 1 and 2. Maximum

TABLE 6: Zero-Point Properties of Solid Krypton and Xenon (Unit: J/mole)

Zero-point properties	Kr		Xe	
	Theory	Semi-empirical	Theory	Semi-empirical
E_z	617	607[c]	536	515[c]
$L_0 = -H$		11158±50[a]		15839±92[a]
		11180±17[b]		15864±28[b]
	11227	11155[c]	15906	16016[c]
		11155±209[d]		16025±209[d]
		11765±50[a]		16354±92[a]
Φ_0	11844	11787±17[b]		16379±_92[b]
		11762[c]	16442	16531[c]
		11762±209[d]		16540±209[d]

[a]Ref. 14, p. 689; [b]Ref. 3; [c]Ref. 15; [d]Ref. 16.

relative differences between calculated and calorimetric values amount at most to −2.8 percent and −4.0 percent for enthalpy and entropy, respectively. Relative differences for enthalpies and entropies are larger than the errors which Schwalbe et al.[3] have mentioned, but decrease with decreasing temperatures. Thermodynamic properties at 0 °K are calculated, and results are presented in Table 6. Since the cohesive energy (L_0) at 0 °K is equal to the negative solid enthalpy ($−H$) at 0 °K, the cohesive energy at 0 °K is calculated using eq. (7). In Table 6, semi-empirecal cohesive energies at 0 °K have been calculated by some investigators from the standard thermodynamic relations using the calorimetric triple point enthalpy values, the experimental heat capacity of the condensed phase along the saturated sublimation pressure curve and the derivatives of the virial coefficients. Heats of sublimation L_0, zero point energies E_z, and the static lattice energies Φ_0, all at 0 °K are interconnected by $\Phi_0 = -L_0 - E_z$, from which Φ_0 are found from tabulated L_0 and E_2. Calculated heats of sub-

TABLE 7: Effects of Gaseous Imperfection Term on the Sublimation Pressure For Solid Kryptom

T (°K)	x	P_{obs}^a (torr)	B_v (cm³/mole)	$(PB_v)^2/2RT$ (cal/mole)	$U_e + D_e x^2(6-5x^2)$ cal/mol	$P_{cal.}$^b (torr)	$P_{cal.}$^c (torr)
115.763	0.9029	547.5	−330 1	0.072076	3521.4	547.3	547.5
115	0.9036	507	−334	0.063753	3518.1	507.0	507.1
114	0.9045	458.1	−340	0.054357	3513.7	458.0	458.1
112	0.9064	371.9	−352	0.040824	3504.5	371.4	371.5
110	0.9082	299.6	−364	0.027617	3495.6	298.8	298.8
108	0.9100	239.5	−388	0.020426	2486.5 •	238.4	238.4

For Solid Xenon

T (°K)	x	P_{obs}^a (torr)	B_v (cm³/mole)	$(PB_v)^2/2RT$^b (cal/mole)	$U_e + D_e(6x^2-5x^4)$ (cal/mole)	$P_{cal.}$^b (torr)	P_{cal}^c (torr)
161.39	0.9002	612.3	−381.4	0.086324	4883.6	612.2	612.4
160	0.9011	554.1	−387.2	0.073491	4877.9	553.8	553.9
158	0.9025	478.6	−395.6	0.057967	4869.0	478.1	478.2
156	0.9039	411.7	−404.2	0.045352	4859.9	411.0	411.1
154	0.9052	352.8	−412.4	0.035123	4851.4	352.1	352.1
152	0.9066	301.2	−423.5	0.027352	4842.1	300.3	300.3
150	0.9079	256.0	−433.8	0.02100	4833.4	254.9	254.9

^a Ref. 1; ^b Calculated from eq. 4 by introducing gaseous imperfection term; ^c Calculated from eq. 4a by neglecting gaseous imperfection term.

limation, zero-point energies and the static lattice energies, all at 0 °K are somewhat larger than semi-empirical values, The differences between calculated and semi-empirical values are almost the same as the quoted errors.

Discussions

The desire to obtain direct and independent physical informations about the condended phases of rare gases from saturated sublimation pressures has lead to a number of increasingly accurate and precise experimental studies in this area. To obtain physical informations, the Salter equation of the sublimation pressure, in particular, has found widespread application[2,9,10]. Salter[9] has derived the following equation of the sublimation pressure (9) by equating the chemical potential of a nonideal vapor to that of a monatomic perfect solid in which the high-temperature limiting form was assumed for the quasiharmonic lattice vibrational free energy.

$$\ln P = -\frac{1}{2}\ln T + [E_0 + P(V_s - B_v)]/RT + 3\ln\omega_g$$
$$+ \frac{1}{2}\ln\left[\left(\frac{m}{2\pi}\right)\frac{1}{k}\right] - e^{-g/kT} \tag{9}$$

where B_v represents the second volume virial coefficient of the vapor, V_s the molar crystal volume, and $\exp(-g/kT)$ corrections for thermal vacancy formation. The parameters generally determined by fitting the Salter equation to sublimation pressures over the wide range of temperatures are the average static lattice energy (E_0) of the atoms at their equilibrium lattice sites and the geometric mean frequency (ω_g) of the lattice vibrational spectrum. Here we should notice that the parameters of the Salter equation based on the perfect crystal structure model are obtained by fitting sublimation pressures over the wide range of temperatures.

The static lattice energy E_0 in the Salter equation is only the average value over the range of temperatures under consideration, and independent of the volume. Nevertheless the static lattice energy is dependent upon the volume. Salter also suggested that the effect of the gas imperfection on the sublimation pressure could be neglected since it's omission would introduce a smaller error in the determination of the static lattice energy (E_0) than the $\exp(-g/kT)$. Our reexamination on the Salter equation (9) indicated an arror that the introduction of the gaseous imperfection does considerably increase the sublimation pressure contrary to facts. To check the influence of the gas imperfection on the sublimation pressure (4), we return to eq. (4a). The data and relevant results of the gaseous imperfections near the triple point are given in Table 7 for krypton and xenon. The second virial coefficients for krypton were calculated from the expression given by Street and Staveley[11] based on the tabulate d data of Dymond and Smith,[12] and are presented in Table 7. The second virial coefficients for xenon have been computed by the following analytic form;

$$B_v(T) = \left(\frac{2}{3}\pi N\right)(r_m)^3 B^*(T^*)$$

where

$$\frac{2}{3}\pi N = 1.26126448, \quad T^* = kT/\varepsilon,$$

$$\text{and } B^*(T^*) = \frac{\exp(1/T^*)}{\sqrt{T^*}}\sum_{i=0}^{4}A_i(\ln T^*)^i$$

The above theoretical second virial coefficients with parameters based on potential of the Barker *et al.*[13] for xenon are presented in Table 7. The sublimation pressures calculated by introducing the gas imperfection near the triple point are presented in Table 7. As shown in Table 7, present

calculated sublimation pressures are in a good agreement with observed values within experimental errors independent of whether the gaseous imperfecition is introduced or not. Although the gas imperfection has the most large effect on the sublimation pressure only near the triple point, the gaseous imperfection does at most decrease the sublimation pressure by 0.1 torr only near the triple point in comparison with vapor assumed to be ideal. The effect of the gaseous imperfection decreases with decreasing temperatures. Therefore effects of the gaseous imperfection on the sublimation pressure and U_e can be neglected, judging from the experimental error even near the triple point. The gaseous imperfection in our eq. (4) decreases the sublimation pressure contrary to the Salter eq. (9). Our consideration of the gaseous imperfection is in agreement with experimental facts. Salter was not justified, therefore, in introducing the gaseous imperfection. Here we should point out that Salter's expression for corrections of the gaseous imperfection had better be replaced by our expression of corrections. The data in Table 7 indicate that the second term in eq. (4a) can be neglected as compared with the first term over the range of temperatures under consideration. As shown in Table 1 and 2, the calculated results of sublimation pressures for solid krypton and xenon are in a good agreement with observed data within an experimental error, although gaseous imperfection has been neglected. This is due to the fact that the gaseous imperfection has a small effect on the sublimation pressure even near the triple point as compared with the experimental accuracy. As shown in Table 3, 4 and 5, the introduction of the gaseous imperfection into expressions of the enthalpy and the entropy of sublimation get the enthalpy and the entropy of sublimation to decrease by 0.2 percent near the triple point, The contributions of the gaseous imperfection on enthalpies and entropies of sublimation amount at most to less than 0.2 percent over the whole temperature range under consideration, and decrease with decreasing temperatures. The contribution of the gaseous imperfection for krypton is almost the same as the measurement uncertainties in magnitude near the triple point, and for xenon is somewhat less than the measurement error near the triple point Therefore we have neglected contributions of the gaseous imperfection on edthalpies and entropies of sublimation. The already mentioned discrepancies of all calculated values such as sublimation pressures, enthalpies and entropies of sublimation, solid enthalpies, solid entropies and zero-point properties from their semi-empirical, calorimetric and obs erved values may be due to an oversimplified model for the potential of inteaction among the atoms in the crystals, an overestimation of the configurational factor, and an ignorance of the volume dependence on the Debye temperature.

Conclusions

The solid partition function, based upon the vacancies-in-solid model, gives equations of sublimation pressure, enthalpy and entropy of sublimation, solid entropy, and

solid enthalpy which may be applied to their prediction over a wide range of temperatures. The Salter's equation requests detailed data of sublimation pressure in advance to estimate parameters, but our equation (4) requests only the triple point temperature, the sublimation pressure and the molar volume at the triple point, the molar volume at 0 °K, and the Debye temperature. Moreover, it should be pointed out that the Salter's equation for the correction the gaseous imperfection causes an increase in the sublimation pressure contrary to the facts, but our correaction of the gaseous imperfection causes little decrease in the sublimation pressure. Our correaction of the gaseous imperfection has little effect on properties such as sublimation pressures, and enthalpies and entropies of sublimation except near the triple point. Estimates of zero-point properties such as the static lattice eneries, heats of sublimation and zero-point eneries all at 0°K, are almost in an agreement with recent semi-empirical values within experimental errors. Relative differences between calculated and semi-empirical values of enthalpies and entropies of sublimation are somewhat larger than experimental errors from 0 °K to the triple point. Relative differences between calculated and calorimetric values of solid enthalpies and entropies are somewhat smaller than calorimetric errors from 0 °K to the triple point. Nevertheless these agreements between present theoretical and experimental values may be interpreted as justifying the vacancies-in-solid model. Accordingly, we may say that the main frame of vacancies-in-solid model is at least in right sign and magnitude. Thus we may deduce some significant features for vacancies-in-solid model as follows:

(1) As far as analysis of differences between the bulk density and the X-ray density and the excess heat capacity done by Peterson *et al.*[18] and Beaumont *et al.*,[7,19] respectively, are correct, this model indicates that it hardly finds the necessity of the anharmocity and the three-body interaction as main contributors to a rapid increase in the discrepancy from normal thermodynamic properties near the triple point. This view is in accordance with the conclusion of Foreman and Lidiard[19] found from C_v analysis on the bsais of an anharmonic Einstein model of the lattice vibration.

(2) This twin-peak frequency model *(θ_D* and *θ_c)* for a perfect crystal gives better results to an estimation of the sublimation pressure, the entropy and the enthalpy of sublimation, the solid enthalpy, and the solid entropy than the Einstein or Debye model

(3) This model indicates that the state of an imperfect oscillator able to have nearest neighbor lattice vacancies is quite different from that of perfect oscillator entirely surrounded by atoms only, since an imperfect oscillator may be able to exist in many positionally degenerate states such vacancy-free state or vacancy-present state.

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Theoretical Study of Isotope and Cation Binding Effects on the Hydration of BDNA

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Theoretical studies of the sodium cation binding and the isotope hydration effects on the static model compound B–DNA have been qualitatively elucidated by using empirical potential energy functions. In the first place, the sodium cations bound to phosphate anions and their hydration scheme have been optimized and have given a reasonable agreement with other theoretical results and experimental studies. In the second stage, the isotope effect on the hydration through the substitution of D_2O for H_2O has been carried out by the same procedure. The stabilization of B–DNA has been explained and compared in terms of the sodium cation binding to phosphate anions and its hydration in both cases of H_2O and D_2O.

Introduction

The effect of environmental factors including metal cation binding and the hydration plays important roles in many aspects of biopolymers. Especially metal ions are considered as a key activator widely in biological processes like transcription, translation[1], and replication, and responsible for catalytic activities of enzymes.[2-4]

Interactions of metal ion with nucleic acids and their constituents to a some extent have been investigated.[5-7] Effects of Na^+ and Mg^{2+} ions on the helix–coil transition of DNA[8,9] and dielectric relaxation[10] have been reported. But only simple cases of interactions between metal cation and phosphat e or dimethylmonophosphate anion and its hydration have been studied by *ab initio* self–consistent field molecular orbital methods.[11-13] And a few Monte Carlo (MC) simulations have been performed for the hydration of the phosphate group of DNA[14]. Isotope effect on the

hydration tends to stabilize not only native protein conformations but also the helical forms of nucleic acids[15]. Hence D_2O substitution lowers the optical absorbance and raises the melting temperature (T_m) values thereby indicating increased helical stability of DNA[16-19] and *t*–RNA[20].

From the theoretical point of view, we have carried out the hydration scheme of the static model compound B–DNA[21] and *t*–RNA[22] without considering counter ion effect. Although in this computation the temperature parameter has not considered, we have obtained the reasonable hydration sites and the stabilization energies due to the hydration, which are in agreement with experimental studies and *ab initio* self–consistent field molecular orbital calculations.

In this paper, we shall elucidate the sodium cation binding scheme of phosphate anions and also incorporated the isotope effect on the hydration of B–DNA by using empirical potential energy functions. The computations