

# Thermodynamic Properties of Platinum Diatomics

PROPERTIES OF PtH, PtC, PtN AND PtO CALCULATED FROM SPECTROSCOPIC DATA

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*Thermodynamic properties of diatomic molecules containing platinum (PtH, PtC, PtN and PtO) have been calculated using spectroscopic data and partition function theory. Values of the Gibbs energy (G), enthalpy (H), entropy (S) and specific heat capacity at constant pressure (C<sub>p</sub>) are presented for each species in the temperature range from 100 K to 3000 K. To obtain the most accurate data, anharmonicity, nonrigidity and stretching effects have been incorporated in the calculations. The variation of these properties with temperature is also discussed in terms of different modes of molecular motion.*

## Introduction

Thermodynamic properties of diatomic transition metal compounds are very important for investigating their thermal behaviour. Recently, these properties have been applied in the fabrication of smart devices using intelligent materials (1) (see (2, 3) for examples using platinum). Transition metal compounds have a wide range of actual and potential applications in materials science because of their relatively high melting points, moderate densities, and resistance to chemical attack. Platinum-containing compounds have been used in nanoscience and nanotechnology. For example, alloys such as iron-platinum (FePt), are used as nanodots (4). Platinum itself is used in a wide range of applications, including catalytic converters for cars, fuel cell electrocatalysts, computer technology, optical communication, missile technology, neurosurgery and medical science (see for example (5)).

The unique properties of platinum generate a high level of interest among scientists. Due to the presence of unpaired *d* electrons, which have a greater angular momentum than *s* and *p* electrons, more energy is needed for the excitation of Pt in the molecular phase. This requires a high energy excitation device such as a gas discharge laser, which leads to experimental difficulties. Thus the experimental study of platinum diatomics is very challenging and expensive.

Scientific groups such as the Scientific Group Thermodata Europe (SGTE), the Joint Institute of

High Temperatures, Russian Academy of Sciences (IVTAN) and, in the U.S.A., the Joint Army-Navy-Air Force (JANAF) Thermochemical Working Group (6) and the National Aeronautics and Space Administration (NASA) (7, 8), are engaged in the critical assessment and compilation of thermodynamic data for different molecular species.

An early contribution to the development of thermodynamic properties was made by Tolman, for diatomic hydrogen (9). The credit for further development of the subject goes to Hicks and Mitchell, for their work on hydrogen chloride (10). Giauque and Overstreet (11) implemented the technique suggested by Hicks and Mitchell for the calculation of these properties for hydrogen, chlorine and hydrogen chloride. They modified the reported theory by using stretching and interaction terms for diatomic molecules. Gordon and Barnes (12) calculated the thermodynamic properties of chlorine (Cl<sub>2</sub>), bromine (Br<sub>2</sub>), hydrogen chloride (HCl), carbon monoxide (CO), oxygen (O<sub>2</sub>) and nitric oxide (NO) molecules. The study of thermodynamic properties of the phosphorous mononitride (PN) molecule was performed by McCallum and Liefer (13). The thermodynamic properties of transition metal alloys were reported by Darby (14). Calculation of the partition function and thermodynamic properties of the rare gas atoms argon, krypton and xenon was performed by Elyutin *et al.* (15). In the domain of theory of thermodynamic properties, Eu (16)

reported Boltzmann entropy, relative entropy and their related values. Chandra and Sharma (17) calculated the partition function for carbon monosulfide (CS) and silicon monoxide (SiO) molecules. Recently Uttam and coworkers (18, 19) estimated the thermodynamic properties of potassium monohalides and alkaline earth metal monohydrides using partition function theory.

The data on thermodynamic properties have been reported for a large number of molecules but a survey of the literature reveals that the values of thermodynamic properties for some diatomic molecules are not yet reported accurately. Therefore we have estimated the thermodynamic properties of platinum monohydride (PtH), platinum monocarbide (PtC), platinum mononitride (PtN) and platinum monoxide (PtO) molecules using spectroscopic data and partition function theory. The choice of the temperature range from 100 K to 3000 K is due to the fact that this range of temperatures covers the applications of platinum from biological sciences to high-temperature chemistry and astrophysics. In the present paper, we report the values of thermodynamic properties Gibbs energy ( $G$ ), enthalpy ( $H$ ), entropy ( $S$ ) and specific heat capacity at constant pressure ( $C_p$ ) for PtH, PtC, PtN and PtO molecules at different temperatures for which these properties are not given in the literature.

## Method of Calculation

A diatomic molecule is associated with translational, rotational, vibrational and electronic motions. Corresponding to these four types of motions, there are four types of energy: translational, rotational, vibrational and electronic energy. Translational motion is due to the three dimensional movement of a molecule in space. Rotational motion is due to the rotation of the molecule as a whole about an axis passing through the centre of gravity and perpendicular to the internuclear axis. In diatomic molecules, atoms are also able to vibrate relative to each other along the internuclear axis and this is the origin of vibrational motion.

Motion of electrons in one atom is perturbed by electronic and nuclear motion in the other atom. Due to this, reshuffling of orbitals takes place and that generates molecular orbitals. This phenome-

non is responsible for electronic motion. The electronic energy,  $\sim 1$  eV to 10 eV, is very high compared to vibrational energy,  $\sim 10^{-2}$  eV, rotational energy,  $\sim 10^{-3}$  eV, and translational energy,  $\sim 10^{-22}$  eV. However, theory shows that below 3000 K molecules are not excited electronically, and electronic motion only plays a significant role above 3000 K. Therefore electronic motion can be neglected below 3000 K.

The contributions of the different motions are summarised on the following page.

## Results and Discussion

The calculated thermodynamic properties namely Gibbs energy, enthalpy, entropy and heat capacity at constant pressure, of PtH, PtC, PtN and PtO molecular gases have been estimated from spectroscopic data and are collected in Tables I–IV. The spectroscopic constants which were used for the calculation of these properties are displayed in Table V (20). PtH is different from PtC, PtN and PtO since it has a  $^2\Delta$  ground state. Therefore we have incorporated the ground state multiplicity in our calculation for the improvement of the results. We have estimated the thermodynamic properties from theoretical spectroscopic data (21) and experimental spectroscopic data (20) for the PtH molecule as shown in Table VI.

From comparison, it is clear that the Gibbs energy has a maximum deviation of 0.12%, enthalpy has 0.11%, entropy has 0.17% and heat capacity has 0.63% up to 2000 K. Ideally it is assumed that rotational and vibrational motions are independent of each other, but in practice they interact with each other. In the present calculation we include this effect by taking the vibrational-rotational partition function instead of the independent rotational and vibrational partition functions. This gives more accurate values of thermodynamic properties than the values obtained from individual rotational and vibrational partition functions. A similar approach has been applied for the calculation of thermodynamic properties of monohalides of potassium (18), and the obtained results were in close agreement with reported values. Accuracy of the data also depends on the vibrational-rotational coupling. If coupling is weak, the stretching con-

## Contributions of the Molecular Motions to the Thermodynamic Properties

### Equations for the Translational Contribution of Thermodynamic Properties

(i) Gibbs energy:	$(G - H_0)_{tran} = -\frac{3}{2}RT \ln m - \frac{5}{2}RT \ln T + 7.2836T$	} (A)
(ii) Enthalpy:	$(H - H_0)_{tran} = \frac{5}{2}RT$	
(iii) Entropy:	$S_{tran} = \frac{5}{2}R + \frac{(G - H_0)_{tran}}{T}$	
(iv) Heat capacity at constant pressure:	$C_{P(tran)} = \frac{5}{2}R$	

### Equations for the Rotational Contribution of Thermodynamic Properties

(v) Gibbs energy:	$(G - H_0)_{rot} = RT \ln \sigma \gamma$	} (B)
(vi) Enthalpy:	$(H - H_0)_{rot} = RT$	
(vii) Entropy:	$S_{rot} = R(1 - \ln \sigma \gamma)$	
(viii) Heat capacity at constant pressure:	$C_{P(rot)} = R$	

### Equations for the Vibrational Contribution of Thermodynamic Properties

(ix) Gibbs energy:	$(G - H_0)_{vib} = RT(1 - e^{-y})$	} (C)
(x) Enthalpy:	$(H - H_0)_{vib} = RT \frac{y}{(e^y - 1)}$	
(xi) Entropy:	$S_{vib} = R \left[ \frac{y}{e^y - 1} - \ln(1 - e^{-y}) \right]$	
(xii) Heat capacity at constant pressure:	$C_{P(vib)} = \frac{Ry^2 e^y}{(e^y - 1)^2}$	

### Equations for the Vibrational-Rotational Contribution of Thermodynamic Properties

(xiii) Gibbs energy:	$(G - H_0)_{vr} = -RT \ln Z_{vr} - R \ln x$	} (D)
(xiv) Enthalpy:	$(H - H_0)_{vr} = RT^2 \frac{\partial}{\partial T}(\ln Z) + R \ln x$	
(xv) Entropy:	$S_{vr} = R[(1 + \ln Z_{vr})] + RT \left[ \frac{\partial}{\partial T}(\ln Z_{vr}) \right]$	
(xvi) Heat capacity at constant pressure:	$C_{P(vr)} = RT \frac{\partial}{\partial T}(\ln Z)$	

Note: The derivation of these equations is given in the Appendix to this paper

stant ( $\alpha_e$ ) is sufficient for the calculation of thermodynamic properties. If coupling is strong, the incorporation of the vibration-rotation constant ( $\gamma_e$ ) gives more accurate data.

It is clear that the specific heat capacity at constant pressure increases with temperature at lower temperatures, but at higher temperatures this becomes constant while Gibbs energy, enthalpy

Table I				
Calculated Thermodynamic Properties of Platinum Monohydride (PtH) Molecule at 1 Atm				
Temperature, $T$ , K	Gibbs energy, $G$ , $\text{kJ mol}^{-1}$	Enthalpy, $H$ , $\text{kJ mol}^{-1}$	Entropy, $S$ , $\text{J mol}^{-1} \text{K}^{-1}$	Specific heat capacity at constant pressure, $C_p$ , $\text{J mol}^{-1} \text{K}^{-1}$
100	17.57	2.08	182.03	29.06
200	36.60	5.29	201.92	29.07
300	57.14	8.52	213.62	29.10
400	78.67	11.18	221.97	29.26
500	100.94	14.33	228.52	29.66
600	123.81	17.31	233.97	30.26
700	147.18	20.25	238.69	30.95
800	171.00	23.19	242.87	31.65
900	195.21	26.13	246.65	32.31
1000	219.78	29.06	250.10	32.89
1100	244.69	32.00	253.27	33.41
1200	269.89	34.95	256.21	33.86
1300	295.38	37.91	258.96	34.25
1400	321.13	40.87	261.53	34.58
1500	347.13	43.84	263.95	34.87
1600	373.36	46.81	266.23	35.11
1700	399.80	49.80	268.39	35.33
1800	426.47	52.80	270.43	35.52
1900	453.33	55.80	272.38	35.68
2000	480.38	58.81	274.24	35.83
2100	507.60	61.84	276.02	35.95
2200	535.00	64.87	277.72	36.06
2300	563.19	66.86	279.62	36.16
2400	590.98	69.77	281.21	36.24
2500	618.93	72.67	282.73	36.33
2600	647.02	75.58	283.63	36.40
2700	675.27	78.49	286.00	36.46
2800	703.65	81.40	287.00	36.51
2900	732.16	84.31	288.33	36.56
3000	760.81	87.21	289.61	36.61

and entropy continue to increase. The heat capacity of any system represents its capacity to contain heat. At lower temperatures only translational motion contributes to this, while as temperature is increased, both rotational and vibrational motions are excited simultaneously and this increases the heat capacity. Beyond a certain temperature, there is no further increase in degrees of molecular motion and this explains the constant value of  $C_p$ .

At the lowest temperature included in this study, 100 K, the  $C_p$  should be very close to the theoretical limit of  $3.5R$ , or  $29.101 \text{ J K}^{-1} \text{ mol}^{-1}$  (where  $R = 8.31457 \text{ J K}^{-1} \text{ mol}^{-1}$ ). In the present case  $C_p$  is less than but very close to  $29.101 \text{ J K}^{-1} \text{ mol}^{-1}$ . This might be due to the fact that quantum mechanics has been used to describe translational motion. This means that the energy of a molecule is considered to be non-zero even at absolute zero.

Table II				
Calculated Thermodynamic Properties of Platinum Monocarbide (PtC) Molecule at 1 Atm				
Temperature, $T$ , K	Gibbs energy, $G$ , $\text{kJ mol}^{-1}$	Enthalpy, $H$ , $\text{kJ mol}^{-1}$	Entropy, $S$ , $\text{J mol}^{-1} \text{K}^{-1}$	Specific heat capacity at constant pressure, $C_p$ , $\text{J mol}^{-1} \text{K}^{-1}$
100	17.22	2.08	201.27	29.07
200	38.47	5.57	221.44	29.33
300	61.25	8.63	233.53	30.50
400	85.07	11.55	242.51	31.96
500	109.69	14.49	249.78	33.20
600	134.98	17.41	255.93	34.14
700	160.84	20.34	261.93	34.82
800	187.20	23.26	265.95	35.32
900	214.00	26.19	270.14	35.70
1000	241.20	29.12	273.93	35.98
1100	268.76	32.05	277.38	36.20
1200	296.65	34.98	280.55	36.38
1300	324.84	37.93	283.48	36.52
1400	353.32	40.88	286.20	36.63
1500	382.05	43.83	288.75	36.72
1600	411.03	46.79	291.13	36.80
1700	440.24	49.74	293.37	36.86
1800	469.67	52.71	295.49	36.91
1900	499.31	55.70	297.50	36.96
2000	529.13	58.65	299.41	37.00
2100	559.15	61.63	301.23	37.03
2200	589.33	64.61	302.96	37.06
2300	620.11	66.86	304.80	37.09
2400	650.67	69.77	306.40	37.11
2500	681.38	72.68	307.94	37.13
2600	712.25	75.59	309.42	37.15
2700	743.27	78.50	310.84	37.16
2800	774.42	81.40	312.21	37.18
2900	885.71	84.31	313.54	37.19
3000	837.13	87.22	314.82	37.20

The enthalpy of an ideal gas depends on temperature and its value increases with temperature. Entropy is a measure of the molecular disorder of a system, and molecules in a system at high temperature are highly disorganised either in terms of their locations or in terms of occupation of their available translational, rotational and vibrational energy states. In contrast, molecules at low temperature have less disorder, and thus have a lower

entropy. Gibbs energy similarly increases with increasing temperature.

## Conclusions

The experimental study of platinum-containing diatomics is expensive and difficult. For the first time, accurate values of thermodynamic properties are reported here for the diatomic molecules PtH, PtC, PtN and PtO. Gibbs energy ( $G$ ), enthalpy ( $H$ ),

Table III				
Calculated Thermodynamic Properties of Platinum Mononitride (PtN) Molecule at 1 Atm				
Temperature, $T$ , K	Gibbs energy, $G$ , $\text{kJ mol}^{-1}$	Enthalpy, $H$ , $\text{kJ mol}^{-1}$	Entropy, $S$ , $\text{J mol}^{-1} \text{K}^{-1}$	Specific heat capacity at constant pressure, $C_p$ , $\text{J mol}^{-1} \text{K}^{-1}$
100	19.86	2.08	205.15	29.07
200	41.25	5.59	225.36	29.52
300	64.18	8.64	237.59	30.99
400	88.16	11.56	246.73	32.55
500	112.96	14.50	254.14	33.76
600	138.44	17.42	260.39	34.61
700	164.50	20.35	265.80	35.23
800	191.06	23.27	270.53	35.66
900	218.07	26.21	274.80	35.99
1000	245.40	29.14	278.59	36.23
1100	273.26	32.09	282.06	36.41
1200	301.36	35.03	285.25	36.56
1300	329.77	37.99	288.20	36.67
1400	358.47	40.95	290.93	36.76
1500	387.42	43.91	293.49	36.84
1600	416.62	46.88	295.88	36.90
1700	446.06	49.86	298.13	36.95
1800	475.71	52.84	300.26	37.00
1900	505.56	55.82	302.28	37.03
2000	535.61	58.81	304.19	37.06
2100	565.85	61.81	306.01	37.09
2200	596.26	64.81	307.75	37.12
2300	627.36	66.77	309.65	37.14
2400	658.16	69.77	311.26	37.16
2500	689.11	72.68	312.80	37.17
2600	720.22	75.59	314.28	37.19
2700	751.47	78.50	315.71	37.20
2800	782.86	81.40	317.09	37.21
2900	814.38	84.31	318.42	37.22
3000	846.04	87.22	319.71	37.23

entropy ( $S$ ) and specific heat capacity ( $C_p$ ) are tabulated for each species over a range of temperatures from 100 K to 3000 K, calculated from spectroscopic data. The utility of this method lies in the fact that it allows the properties of chemically unstable molecules to be predicted. Due to the use of spectroscopic data, the results are highly accurate. The calculated results presented here will be useful to experimental workers in various disciplines, from

biological applications to high-temperature chemistry. This work brings out the usefulness of the results of spectroscopic data in studying thermodynamic properties using statistical mechanics.

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Table IV

## Calculated Thermodynamic Properties of Platinum Monoxide (PtO) Molecule at 1 Atm

Temperature, T, K	Gibbs energy, G, kJ mol <sup>-1</sup>	Enthalpy, H, kJ mol <sup>-1</sup>	Entropy, S, J mol <sup>-1</sup> K <sup>-1</sup>	Specific heat capacity at constant pressure, C <sub>p</sub> , J mol <sup>-1</sup> K <sup>-1</sup>
100	17.52	2.08	204.23	29.08
200	39.06	5.61	224.50	29.79
300	62.17	8.65	236.91	31.55
400	86.34	11.57	246.22	33.15
500	111.35	14.50	253.76	34.28
600	137.04	17.43	260.10	35.05
700	163.32	20.35	265.56	35.59
800	190.12	23.29	270.35	35.96
900	217.36	26.22	274.62	36.23
1000	245.00	29.17	278.47	36.43
1100	273.02	32.12	281.96	36.59
1200	301.36	35.08	285.17	36.71
1300	330.01	38.04	288.13	36.80
1400	358.94	41.01	290.88	36.88
1500	388.14	43.99	293.44	36.94
1600	417.59	46.97	295.84	36.99
1700	447.26	49.96	298.10	37.03
1800	477.15	52.96	300.23	37.07
1900	507.25	55.96	302.26	37.10
2000	537.54	58.97	304.17	37.12
2100	568.03	61.98	306.00	37.14
2200	598.68	63.96	307.75	37.16
2300	630.12	66.87	309.68	37.18
2400	661.17	69.77	311.29	37.19
2500	692.38	72.59	312.84	37.21
2600	723.74	75.59	314.33	37.22
2700	755.24	78.50	315.77	37.23
2800	786.89	81.40	317.15	37.23
2900	818.67	84.31	318.49	37.24
3000	850.58	87.22	319.78	37.25

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Molecules	Molecular weight, $\mu$	Vibrational constant, $\omega_e$ , $\text{cm}^{-1}$	Anharmonicity constant, $\omega_e x_e$ , $\text{cm}^{-1}$	Rotational constant, $B_e$ , $\text{cm}^{-1}$	Stretching constant, $\alpha_e$ , $\text{cm}^{-1}$
PtH	196	2294.68	46.00	7.196300	0.1996000
PtC	207	1051.13	4.86	0.530440	0.0032730
PtN	209	947.00	5.00	0.455708	0.0034481
PtO	211	851.11	4.98	0.382240	0.0028300

From Theoretical Spectroscopic Data				
Temperature, $T$ , K	Gibbs energy, $G$ , $\text{kJ mol}^{-1}$	Enthalpy, $H$ , $\text{kJ mol}^{-1}$	Entropy, $S$ , $\text{J mol}^{-1} \text{K}^{-1}$	Specific heat capacity at constant pressure, $C_P$ , $\text{J mol}^{-1} \text{K}^{-1}$
100	17.59	2.08	182.20	29.06
500	101.03	14.33	228.73	29.77
1000	220.01	29.07	250.43	33.10
1500	347.55	43.87	264.37	35.01
2000	481.00	58.88	274.70	35.92
2500	618.99	74.15	282.91	36.39
3000	760.64	89.66	289.70	36.65
From Experimental Spectroscopic Data				
Temperature, $T$ , K	Gibbs energy, $G$ , $\text{kJ mol}^{-1}$	Enthalpy, $H$ , $\text{kJ mol}^{-1}$	Entropy, $S$ , $\text{J mol}^{-1} \text{K}^{-1}$	Specific heat capacity at constant pressure, $C_P$ , $\text{J mol}^{-1} \text{K}^{-1}$
100	17.57	2.08	182.03	29.06
500	100.94	14.33	228.52	29.66
1000	219.78	29.06	250.10	32.89
1500	347.13	43.84	263.95	34.87
2000	480.38	58.81	274.24	35.83
2500	618.93	72.67	282.73	36.33
3000	760.81	87.21	289.70	36.61

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## Appendix

### Method of Calculation for the Individual Partition Functions

According to the non-rigid rotator model, the rotational energy of a diatomic molecule is given by Equation (xvii):

$$E_{rot} = [B_e J(J+1) - D_e J^2 (J+1)^2] hc \quad (\text{xvii})$$

where  $E_{rot}$  is the rotational energy,  $J$  is the rotational quantum number,  $h$  is Planck's constant,  $c$  is the velocity of light,  $B_e$  is the rotational constant and  $D_e$  is the centrifugal constant.

The expression for vibrational energy,  $E_{vib}$ , according to the anharmonic oscillator model is given in Equation (xviii):

$$E_{vib} = \left[ \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 \right] hc \quad (\text{xviii})$$

where  $\omega_e$  is the vibrational constant,  $\omega_e x_e$  is the anharmonicity constant and  $v$  is the vibrational quantum number.

Total energy of a diatomic molecule can be written as Equation (xix):

$$E_t = E_{rot} + E_{vib} + E_{ele} + E_{tran} \quad (\text{xix})$$

where  $E_t$  is total energy,  $E_{rot}$  is rotational energy,  $E_{vib}$  is vibrational energy,  $E_{ele}$  is electronic energy and  $E_{tran}$  is translational energy.

The partition function,  $Z$ , contains all the relevant information of any physical system. It is approximately equal to the number of quantum states having energies below the thermal energy available to the molecule in the given volume. The partition function can be expressed as Equation (xx) (22, 23):

$$Z = \sum_i g_i e^{-\frac{E_i}{k_B T}} \quad (\text{xx})$$

where  $g_i$  is the degeneracy of the  $i$ th energy level,  $E_i$  is the energy of the  $i$ th level,  $k_B$  is the Boltzmann constant,  $T$  is absolute temperature in Kelvin and  $i$  ranges over all quantum states.

Four types of energy give rise to four types of partition function. Thus the total partition function of the system,  $Z_t$ , can be written as Equation (xxi):

$$Z_t = Z_{tran} Z_{rot} Z_{vib} Z_{ele} \quad (\text{xxi})$$

where  $Z_{tran}$ ,  $Z_{rot}$ ,  $Z_{vib}$  and  $Z_{ele}$  represent the partition functions for translational energy, rotational energy, vibrational energy and electronic energy respectively.

The contributions of the individual partition functions to the thermodynamic properties can be calculated separately and are given in the following sections.

### Translational Partition Function

Translational energy for a particle of mass  $m$  in a cuboid of sides  $p$ ,  $q$  and  $r$  can be written as Equation (xxii):

$$E_{\text{tran}} = \frac{h^2}{8m} \left( \frac{n_x^2}{p^2} + \frac{n_y^2}{q^2} + \frac{n_z^2}{r^2} \right) \quad (\text{xxii})$$

where  $n_x$ ,  $n_y$  and  $n_z$  are the various quantum states.

The translational partition function corresponding to this energy can be written as Equation (xxiii):

$$Z_{\text{tran}} = \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{-\frac{h^2}{8mk_B T} \left( \frac{n_x^2}{p^2} + \frac{n_y^2}{q^2} + \frac{n_z^2}{r^2} \right)} \quad (\text{xxiii})$$

Here we take an approximation and change this summation into integration to obtain Equation (xxiv):

$$Z_{\text{tran}} = \int e^{-\frac{h^2}{8mk_B T} \left( \frac{n_x^2}{p^2} \right)} dn_x \int e^{-\frac{h^2}{8mk_B T} \left( \frac{n_y^2}{q^2} \right)} dn_y \int e^{-\frac{h^2}{8mk_B T} \left( \frac{n_z^2}{r^2} \right)} dn_z \quad (\text{xxiv})$$

Using the standard result of integration, we get Equation (xxv):

$$Z_{\text{tran}} = \left[ \frac{p}{2} \left( \frac{8\pi mk_B T}{h^2} \right)^{\frac{1}{2}} \right] \cdot \left[ \frac{q}{2} \left( \frac{8\pi mk_B T}{h^2} \right)^{\frac{1}{2}} \right] \cdot \left[ \frac{r}{2} \left( \frac{8\pi mk_B T}{h^2} \right)^{\frac{1}{2}} \right] \quad (\text{xxv})$$

Using  $V = pqr$  where  $V$  is the volume of the enclosure gives Equation (xxvi):

$$Z_{\text{tran}} = V \left( \frac{2\pi mk_B T}{h^2} \right)^{\frac{3}{2}} \quad (\text{xxvi})$$

Dividing both sides of this expression by the number of particles,  $N$ , we obtain Equation (xxvii):

$$\frac{Z_{\text{tran}}}{N} = \left( \frac{2\pi mk_B T}{h^2} \right)^{\frac{3}{2}} \frac{V}{N} \quad (\text{xxvii})$$

We consider  $Z_{\text{tran}}/N$  instead of  $Z_{\text{tran}}$  as the quantity  $Z_{\text{tran}}/N$  is an intensive quantity and depends on the concentration,  $N/V$ , whereas  $Z_{\text{tran}}$  itself is proportional to  $V$  and independent of the number of particles.

Using the ideal gas equation, Equation (xxvii) can be written as Equation (xxviii):

$$\frac{Z_{\text{tran}}}{N} = \left( \frac{2\pi mk_B T}{h^2} \right)^{\frac{3}{2}} \frac{k_B T}{P_0} \quad (\text{xxviii})$$

where  $P_0$  denotes one atmospheric pressure ( $1.01325 \times 10^5 \text{ N m}^{-2}$ ).

Using the above partition function, the translational contribution of the various thermodynamic properties can be estimated by the set of Equations (A) (22), where  $H_0$  represents enthalpy at a temperature of 298.15 K, and  $R$  is the gas constant.

### Rotational Partition Function

Partition function theory shows that the rotational partition function can be written as Equation (xxix):

$$Z_{\text{rot}} = \frac{1}{\sigma y} \sum_J (2J+1) e^{-yJ(J+1)} \quad (\text{xxix})$$

where  $y$  is a constant given by Equation (xxx):

$$y = 4.7994 \frac{B_e}{T} \quad (\text{xxx})$$

and  $\sigma$  is the symmetry number which has a value of 2 for a homonuclear molecule and 1 for a heteronuclear molecule. The symmetry number is defined as the number of regions of phase space included in the partition function calculation, which differ only by the exchange of indistinguishable particles. In quantum theory the symmetry number arises from the fact that only a fraction of the rotational states are allowed in a symmetrical molecule and this fraction is  $1/\sigma$ .

If  $y$  is small, the summation changes into integration and we have Equations (xxxii) to (xxxiii):

$$Z_{\text{rot}} = \frac{1}{\sigma} \int (2J+1) e^{-yJ(J+1)} dy \quad (\text{xxxii})$$

$$Z_{\text{rot}} = \frac{1}{\sigma y} \quad (\text{xxxiii})$$

$$Z_{rot} = \frac{T}{4.7994\sigma B_e} \quad (\text{xxxiii})$$

Using the Euler-Maclaurin formula, we get Equation (xxxiv):

$$Z_{rot} = \frac{1}{\sigma y} \left( 1 + \frac{y}{3} + \frac{y^2}{15} + \dots \right) \quad (\text{xxxiv})$$

Using this partition function, the rotational contribution in the thermodynamic properties may be obtained from the relations in Equation set (B) (22).

### Vibrational Partition Function

For a one-dimensional harmonic oscillator, energy levels are given by Equation (xxxv):

$$E_{vib} = hf \left( v + \frac{1}{2} \right) \quad (\text{xxxv})$$

where  $f$  is the frequency of molecular vibration given by Equation (xxxvi):

$$f = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{\frac{1}{2}} \quad (\text{xxxvi})$$

in which  $k$  is the force constant and  $\mu$  is the reduced mass of the molecule, and  $v = 0, 1, 2, 3$  etc. For  $v = 0$ , the oscillator has zero point energy,  $E_0$ , which from Equation (xxxv) is equivalent to  $hf/2$ .

It is convenient to subtract the zero energy state ( $v = 0$ ), except for problems involving isotopic molecules. Then we have Equation (xxxvii):

$$E_v - E_0 = hf v = hc\omega_e v \quad (\text{xxxvii})$$

Using Equation (xxxviii):

$$\frac{E_v - E_0}{k_B T} = y v \quad (\text{xxxviii})$$

in which  $y$  is defined by Equation (xxxix):

$$y = \frac{hf}{k_B T} = 4.7994 \frac{B_e}{T} \quad (\text{xxxix})$$

Theory shows that the vibrational partition function can then be written as Equation (xl):

$$Z_{vib} = \sum_v e^{-y v} \quad (\text{xl})$$

From which we obtain Equation (xli):

$$Z_{vib} = \frac{1}{(1 - e^{-y})} \quad (\text{xli})$$

The vibrational contribution of the thermodynamic properties is derived using this partition function by the expressions in Equation set (C) (22).

### Vibrational-Rotational Partition Function

If we assume that the rotational and vibrational motions do not interact with each other, the total partition function will be the multiple of the rotational, vibrational and translational partition functions. But in real cases, both types of motion do affect each other and stretching and anharmonicity also need to be considered. Then total internal energy can be given as Equation (xlii):

$$E = \omega_0 v - \omega_e x_e \left( v + \frac{1}{2} \right) + B_e J(J+1) - D_e J^2 (J+1)^2 - \alpha_e \left( v + \frac{1}{2} \right) J(J+1) \quad (\text{xlii})$$

Using Equations (xliii), (xliv) and (xlv):

$$B_o = B_e - \frac{\alpha_e}{2} \quad (\text{xliii})$$

$$\omega_0 = \omega_e - 2\omega_e x_e \quad (\text{xlv})$$

$$\omega_0 x = \omega_e x_e \quad (\text{xlv})$$

where  $x$  represents the multiplicity of the ground state,  $\alpha_e$  is the stretching constant,  $B_0$  is the ground state rotational constant and  $\omega_0$  is the actual separation of the first two vibrational levels, and substituting into the energy expression in Equation (xlii) this can then be written as Equation (xlvi):

$$E = \omega_0 v - \omega_0 x v (v-1) + J(J+1)[B_0 - D_e J(J+1) - \alpha_e v] \quad (\text{xlvi})$$

For simplification, we further substitute Equations (xlvi), (xlvii), (xlix) and (l):

$$u = \frac{hc\omega_0}{k_B T} \quad (\text{xlvii})$$

$$a = \frac{hcB_0}{k_B T} \quad (\text{xlviii})$$

$$\beta = \frac{D_e}{B_0} \quad (\text{xlix})$$

$$\delta = \frac{\alpha_e}{B_0} \quad (\text{l})$$

Then we have Equation (li):

$$E = uv[1 - (v-1)x] + J(J+1)a[1 - \beta J(J+1) - v\delta] \quad (\text{li})$$

Corresponding to this energy, the vibrational-rotational partition function,  $Z_{vr}$ , be simplified as Equation (lii) (16, 17):

$$Z_{vr} = \frac{1}{\sigma a(1-e^{-u})} \left[ 1 + \frac{2\beta}{a} + \frac{\delta}{e^u - 1} + \frac{2xu}{(e^u - 1)^2} + \frac{a}{3} + \frac{a^2}{15} \right] \quad (\text{lii})$$

Or Equation (liii):

$$Z_{vr} = Z_I Z_C \quad (\text{liii})$$

where  $Z_I$  represents the ideal partition function which is valid for the rigid rotator harmonic oscillator model and  $Z_C$  represents the corrected partition function and gives the contribution due to centrifugal stretching, nonrigidity and anharmonicity of the diatomic molecule. Expressions for  $Z_I$  and  $Z_C$  can be written as Equations (liv) and (lv):

$$Z_I = \frac{1}{\sigma a(1-e^{-u})} \quad (\text{liv})$$

$$Z_C = \left[ 1 + \frac{2\beta}{a} + \frac{\delta}{e^u - 1} + \frac{2xu}{(e^u - 1)^2} + \frac{a}{3} + \frac{a^2}{15} \right] \quad (\text{lv})$$

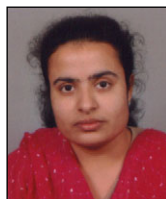
This partition function can be used to estimate the contribution of vibrational-rotational motion to the Gibbs energy, enthalpy, entropy and heat capacity by the formulae in Equation set (D) (22).

Finally, the thermodynamic properties like Gibbs energy, enthalpy, entropy and heat capacity of platinum molecular gases are calculated by adding the translational contribution and the vibrational-rotational contribution.

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