PREDICTION OF ENTROPY OF VAPORIZATION OF INORGANIC GASES

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ABSTRACT

Generalized correlations have been developed to predict entropy of vaporization for inorganic gases based respectively on (i) molacular volume at boiling point, (ii) normal boiling point (iii) molecular weight.

1. INTRODUCTION

ARGON is non-polar, non-reactive and devoid of any quantum mechanical effect and hence it is ideally suited to be used as a reference substance for prediction of thermodynamic properties of organic and inorganic compounds It has been shown earlier[1] that the entropy of vaporization of hydrocarbons at various reduced temperntures can be predicted accurately using ARGON as a reference substance. A similar procedure is being extended, in this work, for inorganic gases. Both non polar and highly polar gases are considered and correlations are given for both these types of gases.

Entropy of vaporization of argon (ΔS_A) and various inorganic Gases (ΔS_S) from the literature[2-9] were plotted against temperatures, from which the smoothed values of ΔS_A ΔS_S at the required reduced temperatures were obtained. The reduced temperatures for the gases considered generally varied between 1.0 and 0.60. When these values of entropy of vaporization of Argon were plotted against the entropy of vaporization of one inorganic gas at various reduced temperatures a good linear relationship was obtained Similar good linear relationships were observed for all the 12 inorganic gases considered in this work All these lines pass through the origion, but the slopes were found to vary with the chemical species.

To arrive at a generalised equation to predict ΔS_S for all gases and for all temperature ranges, attempts were made to correlate these slopes with some easily assessible physical properties of these substances. Following the successful correlation[1] obtained for the case of hydrocarbons, attempts were made to correlate slopes with either molecular weights or the normal boiling points. But both of them failed to show any general pattern with which one could base the generalised equation to predict ΔS_S.

However when these values of slopes were plotted against the molecular volume at its boiling point of these substances on semi-logarithmic co-ordinates they showed a definite pattern. All the diatomic gases fell in a good straight line and all the polyatomic gases fell in a different straight line. Considering the degrees of freedom for mono, di, and polyatomic gases to be 3, 5 and 6 respectively and the mean energy of a molecule is proportional to $(\frac{1}{2}f)$, where f is the degree of freedom, a correction was available for the slopes. These values were divided by $(\frac{1}{2}f=k)$ and plotted against the molecular volumes when a good linear relationship was obtained for both diatomic and polyatomic gases. A generalised equation to predict the entropy of vaporization of inorganic gases at various temperatures was obtained, which is

$$\Delta S_S = K\left[(0.1716 \log V_b + 0.1651)\ \Delta S_A\right] \qquad [1]$$

where $K = 2.5$ for diatomic gases and 3.0 for polyatomic gases.

Equation 1 was tested for all the 12 gases considered in this work. Table 1 gives the physical properties of these substances. Literature values of $\Delta S_A^{(2)}$ and $\Delta S_S^{(2-9)}$ and the calculated values of ΔS_S by using equation 1 for different reduced temperatures and the percentage errors are given in Table 2. Equation 1 does not give a good fit for highly polar gases like NH_3, H_2S, H_20 and N_2H_4. The entropy of vaporization at different temperatures can be predicted within an over all average error of 2.7% for non-polar gases, by using equation 1. In no case, for these non-polar gases, the average error exceeds 5.4%.

The boiling point correlation, although failing to predict for the non-polar gases, gave accurate prediction for the highly polar gases. The respective equations for normal boiling point correlation and molecular weight correlation from reference (1), are

$$\Delta S_A = [1.069 - 1.029 \times 10^{-3}\, T_b]\ \Delta S_S \qquad [2]$$

and

$$\Delta S_A = [0.926 - 2.326 \times 10^{-3}\, M]\ \Delta S_S \qquad [3]$$

Equation [2] predicts the entropy of vaporization of highly polar gases, (Table 2) within an over-all average error of 3.1 %. Equation 3 is not recommended for both polar and non polar inorganic gases.

Equation 1 is recommended for non-polar gases and Equation 2 is recommended for polar gases, to predict the entropy of vaporization of inorganic gases at different temperatures, within an average error of 3.0%.

TABLE I

Properties of the Compounds

	Compounds	Molecular Volume at Boiling Point	Normal Boiling Point	Molecular weight
		(V_b)	(T_b)	(M)
1.	Nitrogen	31.2	77.35	28.02
2.	Oxygen	25.6	90.16	32.00
3.	Carbon monoxide	30.7	81 66	28 01
4.	Chlorine	45.5	238 .6	70.91
5.	Carbon dioxide	34.0	194.71	44.01
6.	Sulfur dioxide	44 8	263 16	64 07
7.	Nitrous oxide	36.4	183.66	44.02
8.	Phosgene	69.5	280.72	98.92
9.	Ammonia	25.8	239.81	17 03
10.	Hydrogen sulfide	32 9	213.56	34.08
11.	Water	18.9	373.16	18.02
12.	Hydrazine	46.0	386.66	32.05

TABLE 2

Calculated and Experimental values of Entropy of Vaporization for various Inorganic Gases

	Tr.	ΔS_A (Ref. 2)	ΔS_S Lit.	ΔS_S Cal. (Eq. 1)	%Div.	ΔS_S Cal. (Eq. 2)	%Div.	ΔS_S Cal. (Eq. 3)	%Div
Nitrogen (Ref 2)	0 96	4 46	4.88	4 70	3.7	4 51	7.6	5 18	6 1
	0 94	5.23	5 92	5 51	6.9	5.29	10.6	6.08	2.7
	0 92	5 97	6.80	6 29	7.5	6 03	11.3	6.94	2.0
	0 88	7.41	8 27	7.81	5 6	7 49	9.4	8.61	4 1
	0 84	8 74	9 67	9.19	5 0	8 83	8.7	10 15	5.0
	0 80	10 02	10 95	10 56	3.6	10.13	7.5	11 64	6 3
	0 76	11.33	12.23	11.94	2.4	11.45	6 4	13.16	7.6
	0 72	12 63	13.44	13 31	1.0	12 77	5.0	14.67	9.1
	0 68	14 00	14.27	14.75	3.4	14.15	0.8	16.26	13.9
				Average	4.3	Average	7.5	Average	6.3
Oxygen (Ref. 3)	0 96	4 46	4 78	4 54	5.0	4.57	4.4	5 24	9.6
	0.94	5.23	5 71	5.32	6.8	5.36	6.1	6 14	7 5
	0.92	5.97	6.46	6.07	6.0	6.12	5 3	7.01	8 5
	0.88	7.41	7 70	7.53	2.2	7.59	1 4	8.70	13 0
	0 84	8 74	9 04	8.89	1.6	8.95	1 0	10.26	13.4
	0.80	10 02	10.17	10 19	0.2	10 26	0.9	11.77	15.7
	0 76	11.33	11.86	11.52	2.9	11.61	2.1	13.30	12.1
	0.72	12.63	12 81	12.84	0.2	12 94	1.0	14 83	15 8
	0.68	14.00	14.13	14.24	0.8	14.34	1.5	16.44	16.3
	0 64	15.42	15.63	15 68	0.3	15.80	1.1	18.11	15.9
				Average	2.6	Average	2.5	Average	12 8

TABLE 2—(*contd.*)

	Tr.	ΔS_A (Ref. 2)	ΔS_S Lit.	ΔS_S Cal. (Eq. 1)	%Div.	ΔS_S Cal (Eq. 2)	%Div.	ΔS_S Cal. (Eq. 3)	%Div.
Carbon monoxide (Ref. 2)	0.96	4.46	4.53	4.69	3.5	4.53	0.0	5.18	14.3
	0.94	5.23	5.67	5.50	3 0	5.31	6.3	6.08	7.2
	0.92	5 97	6 63	6.27	5 4	6.06	8.6	6.94	4.7
	0.88	7.41	8 07	7.79	3.5	7.52	6 8	8 61	6 7
	0.84	8.74	9.24	9.18	0 6	8 87	4 0	10.15	9.8
	0.80	10 02	10 44	10 53	0 9	10.17	2.6	11 64	11 5
	0.76	11.33	11.82	11 90	0.7	11 50	2.7	13.16	11 3
	0.72	12 63	13.24	13.27	0.2	12.82	3 2	14.67	10 8
	0.68	14 00	14.85	14.71	0.9	14.21	4 3	16.24	9 5
				Average	2.1	Average	4.3	Average	9.5
Chlorine (Ref. 4)	0.96	4.46	5.05	5 01	0.8	5.41	7.1	5.86	16 8
	0.94	5.23	6.07	5.88	3 1	6.35	4.6	6.87	13.2
	0 92	5.97	6.96	6.71	3.6	7.25	4.2	7.84	12.6
	0.88	7.41	8.56	8 33	2.7	9 00	5.1	9.74	13.7
	0 84	8 74	9 96	9 82	1.4	10 61	6.5	11 48	15 3
	0 80	10.02	11.28	11.26	0.2	12.17	7.9	13.16	16.7
	0 76	11.33	12.63	12 74	0 9	13.76	8.9	14.89	17.9
	0.72	12.63	13.97	14 20	1 6	15.34	9.8	16.59	18.7
	0 68	14 00	15.44	15.74	1.9	17 00	10.1	18 39	19.1
	0.64	15.42	17.13	17.33	1.2	18 73	9.3	20 26	18 3
	0.60	16.98	19.06	19 09	0.1	20.62	8.2	22.31	17.0
			Average	1.6		Average	7.4	Average	16.3

TABLE 2—(*contd.*)

	Tr.	ΔS_A (Ref 2)	ΔS_S Lit.	ΔS_S Cal. (Eq. 1)	%Div.	ΔS_S Cal (Eq. 2)	%Div.	ΔSS Cal. (Eq 3)	%Div.
Carbon dioxide (Ref. 2)	0.96	4.46	5.73	5 73	0.0	5.13	10 5	5 42	5.4
	0 94	5.23	6.86	6 71	2.2	6.02	12 2	6.35	7.4
	0.92	5.97	7.88	7.66	2.8	6.87	12.8	7.25	8 0
	0.88	7.41	9.77	9.51	2 7	8 53	12.6	9.00	7.9
	0.84	8.74	11.46	11 22	2.1	10 06	12.2	10.61	7.4
	0 80	10.02	13 07	12.86	1.6	11.54	11.7	12.17	6.9
	0 76	11.33	14.72	14.54	1.2	13.04	11.4	13 76	6 5
	0.72	12.63	16.51	16.21	1 8	14.54	11.9	15.33	7.1
	0.68	14.00	18.40	17 97	2.3	16.12	12.4	17 00	7.6
				Average	1.8	Average	12.0	Average	7.1
Sulphur dioxide (Ref. 5)	0 96	4.46	5.74	6.00	4 5	5.59	2.6	5 74	0.0
	0.94	5.23	7.02	7.04	0.3	6 55	6.7	6 73	4.1
	0.92	5.97	8 13	8.03	1.2	7.48	8 0	7 68	5.5
	0.88	7.41	10 05	9 97	0 8	9 28	7.7	9 54	5.1
	0.84	8.74	11.78	11.76	0.2	10.95	7.0	11.25	4.5
	0 80	10 02	13.50	13.48	0.1	12.55	7 0	12.90	4.4
	0.76	11.33	15.26	15.24	0.1	14.19	7.0	14 58	4.4
	0.72	12.63	17.06	16.99	0.4	15 82	7.3	16.26	4 7
	0 68	14.00	18.98	18 84	0.7	17.54	7.6	18.02	5 0
	0.64	15.42	21.05	20.75	1.4	19.32	8.2	19.85	5 7
				Average	1.0	Average	6.9	Average	4.3

TABLE 2—(*contd*)

	Tr.	ΔS_A (Ref. 2)	ΔS_S Lit.	ΔS_S Cal. (Eq. 1)	%Div.	ΔS_S Cal (Eq. 2)	%Div.	ΔS_S Cal (Eq. 3)	%Div.
Nitrous oxide (Ref. 6)	0 96	4.46	6.06	5.80	4.3	5.07	16.3	5.41	10.7
	0 94	5.23	7.08	6.79	4.1	5.94	16.1	6.35	10.3
	0.92	5.97	7.96	7.75	2.6	6 78	14.8	7.25	8 9
	0.88	7.41	9.63	9.62	0.0	8.42	12 6	9.00	6 5
	0.84	8 74	11.21	11.35	1.2	9.93	11 4	10.61	5.3
	0.80	10.02	12.76	13.02	2.0	11.39	10.7	12.16	4.7
	0.76	11.33	14.36	14.71	2.4	12.87	10.4	13.76	4.2
	0 72	12.63	16.03	16 40	2.3	14.35	10.5	15.33	4.4
	0.68	14.00	17.74	18.18	2.5	15.91	10 3	17.00	4.2
	0.64	15.42	19.52	20 03	2.6	17 52	10 2	18.72	4 1
	0 60	16.98	21.33	22.06	3.4	19.30	9.5	20 62	3.3
				Average	2.5	Average	12.1	Average	6.1
Phosgene (Ref. 7)	0 96	4.46	5 98	6.44	7.7	5.72	4.3	6.41	7.2
	0 94	5.23	7.32	7 55	3.1	6.70	8.5	7.51	2 6
	0.92	5 97	8.53	8.62	1.0	7 65	10 3	8 58	0.6
	0.88	7.41	10.64	10 70	0 6	9 50	10 7	10 55	0 1
	0.84	8.74	12 33	12.62	2.3	12 20	9.2	12.56	1.9
	0 80	10.02	13.75	14.46	5.2	12.84	6.6	14.40	4.7
	0.76	11.33	15 36	16 35	6 4	14 52	5.5	16.28	6 0
	0 72	12.63	16.87	18.23	8.1	16.19	4.0	18 15	7.6
	0 68	14 00	18.44	20.21	9 6	17 94	2.7	20 12	9 1
	0.64	15 42	20.17	22.26	10.4	19.76	2 0	22.16	9.9
				Average	5.4	Average	6.4	Average	5.0

TABLE 2.—(CONTD.)

	Tr.	ΔS_A (Ref. 2)	ΔS_S Lit.	ΔS_S Cal. (Eq. 1)	%Div.	ΔS_S Cal. (Eq. 2)	%Div.	ΔS_S Cal. (Eq. 3)	%Div.
Ammonia (Ref. 2)	0.96	4 46	5.44	5.45	0.2	5 42	0.4	5.03	7.5
	0.94	5.23	6.69	6.39	4 5	6 36	4 9	5.90	11.8
	0 92	5 97	7.78	7.30	6.2	7.26	6.7	6.74	13 3
	0.88	7.41	9.68	9 05	6.5	9 01	6 9	8 36	13.6
	0.84	8.74	11.46	10.68	6 8	10.63	7.2	9 86	14 0
	0.80	10 02	13.12	12.24	6 7	12.19	7 1	11.30	13.9
	0.76	11.33	14 83	13.85	6.6	13.78	7.1	12.78	13.8
	0.72	12.63	16.60	15.43	7.0	15 36	7 5	14.25	14.1
	0 68	14.00	18 50	17 11	7.5	17.03	7 9	15.79	14.6
	0.64	15.42	20 53	18.84	8 2	18.75	8.7	17.40	15.2
					Average 6.0		Average 6.4		Average 13 2
Hydrogen Sulfide (Ref. 6)	0.96	4.46	5.05	5.69	12.7	5.25	4.0	5.27	4.3
	0 94	5.23	6.20	6.67	7.6	6.16	0.6	6.18	0.3
	0.92	5 97	7.13	7.62	6.9	7 03	1.4	7 05	1.1
	0.88	7.41	8 66	9 46	9.2	8 72	0.7	8.75	1 0
	0 84	8.74	10.15	11.16	9 9	10.29	1.4	10.32	1.7
	0 80	10.02	11.56	12.79	10.6	11 80	2.1	11 83	2.3
	0 76	11.33	13.00	14.46	11.2	13.34	2.6	13 38	2.9
	0.72	12.63	14.52	16.12	11 0	14.87	2.4	14 92	2.7
	0 68	14.00	16.11	17.87	10.9	16.48	2.3	16.53	2.6
	0.64	15.42	17.87	19 68	10.1	18.16	1 6	18 21	1.9
					Average 10 0		Average 1.9		Average 2.1

TABLE 2—(*contd.*)

	Tr.	ΔS_A (Ref. 2)	ΔS_S Lit.	ΔS_S Cal. (Eq 1)	%Div.	ΔS_S Cal. (Eq. 2)	%Div.	ΔS_S Cal. (Eq. 3)	%Div.
Water (Ref. 8)	0.96	4 46	6.36	5.14	19.2	6.51	2.3	5.04	20.7
	0.94	5.23	7.64	6 02	21.2	7.63	0.1	5 91	22.6
	0 92	5 97	8.76	6.88	21 5	8.72	0.5	6 75	22.9
	0 88	7.41	10 80	8 54	20.9	10 82	0.2	8.38	22 4
	0 84	8.74	12 66	10.07	20.4	12.76	0.8	9 88	21.9
	0 80	10 02	14.47	11 54	20 2	14 63	1.1	11.33	21 7
	0.76	11.33	16.28	13 06	19.8	16.54	1.6	12 81	21 3
	0.72	12.63	18 16	14.56	19 8	18 44	1.5	14 28	21.4
	0 68	14.00	20 13	16.14	19 8	20.44	1.5	15 83	21.4
	0.64	15 42	22 23	17 77	20.1	22 51	1.2	17 44	21.5
	0.60	16.98	24.56	19.57	20.3	24.79	0.9	19.21	21.8
				Average	20.3	Average	1.1	Average	21.8
Hydrozine (Ref. 9)	0 96	4.46	7.04	6.03	14.3	6 64	5.7	5 24	25.5
	0.94	5 23	8.42	7 07	16.0	7 79	7.5	6 14	27.0
	0 92	5.97	9.61	8.07	16.0	8.89	7.5	7.01	27 0
	0 88	7.41	11.60	10 01	13.7	11.04	4.8	8.70	25 0
	0.84	8.74	13.47	11 81	12.3	13.62	3.3	10.26	23 8
	0.80	10.02	15.18	13.54	10 8	14 93	1.6	11.77	22.5
	0.76	11 33	17.02	15.31	10.0	16.88	0.8	13.31	21.8
	0.72	12 63	18 87	17.07	9.5	18.82	0 3	14.83	21.4
	0.68	14.00	20 93	18.92	9.6	20.86	0 3	16.44	21 4
	0.64	15.42	23 06	20.84	9.6	22.98	0.3	18.11	21.5
	0.60	16.98	25.26	22.94	9.2	25.30	0.1	19.94	21.1
				Average	11.9	Average	2.9	Average	23.5

Nomenclature

ΔS_S – Entropy of vaporization of the substances (Cal/mole $^\circ K$)

ΔS_A – Entropy of vaporization of Argon (Cal/mole $^\circ K$)

V_b – Molecular volume at its boiling point (cc/g mole)

T_b – Normal boiling point $^\circ K$

M – Molecular weight

$k = \frac{1}{2} f$ ($f = 5$ for diatomic gases and $f = 6$ for polyatomic gases)

f = Degrees of freedom

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