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RELATION BETWEEN THE VAPORIZATION HEAT AND THE FIRST IONIZATION POTENTIAL IN SERIES OF LIQUIDS AT NORMAL BOILING POINT

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ABSTRACT

It is shown that a general relationship exists between the latent heat of vaporization and the first ionization potential for liquids at the normal boiling point. The generalized parabolic relation is:

$$Y = 2.478 + 0.07X - 0.017X^2$$

where $Y = \ln(hc\omega/T_B)$ and $X = \ln(\Delta H_v/RT_B)$, such that ω is the first ionization potential expressed in reciprocal centimeters; while ΔH_v is the latent heat of vaporization at the normal boiling point temperature T_B.

INTRODUCTION AND DISCUSSION

The purpose of this work is to study the possible relation between the latent heat of vaporization and the first ionization potential of the molecule. It is well known that the first ionization potential of the molecule represents the exchange energy of a delocalized electron which comes from all over the molecule and not from a particular lone pair or bond*. But the interaction (or chemical bonding) between any two atoms in substance can be related to the potential at which their outer electrons can be removed (electronegativity concept). This potential increases with the number of s and p valency electrons.

If we consider the evaporation process as a disruption of the existing various liquid intermolecular bonds, and if we accept that the ionization potential of the molecule is related to chemical (bond forming) properties of the element as implied through the cited molecular orbital calculation methods, we may well conceive that the measure of the energy of disruption of the liquid intermolecular bonds, or the latent heat of vaporization is related to the ionization potential of the liquid-forming molecule. In this case the connection is found through establishing a relation between

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*This thought characterizes the ionization energy calculation for molecules and is expressed through the classical work of Mulliken[1,2] on molecular orbital calculations, and later methods for calculating the ionization energies of the molecule as proposed for instance by Hall[3] and Lennard-Jones and Hall[4] and used by Brailsford and Ford[5] in the case of linear alkanes.

the natural logarithm of the dimensionless entropy of evaporation $\ln(\Delta H_v/RT_B)$ referred to the normal boiling temperature; and the natural logarithm of the ratio of two energies: the "radiation" energy represented by the first ionization potential of the molecule to the thermal energy of liquid at the evaporation temperature, written as $\ln(hc\omega/kT_B)$.

Using the available data (Tables 1–4, Fig. 1), the following generalized parabolic equation was obtained:

$$Y = 2.478 + 0.072X - 0.017X^2 \qquad (1)$$

where $Y = \ln(\Delta H_v/RT_B)$ and $X = \ln(hc\omega/kT_B)$, such that ω is the first ionization potential of the element or molecule expressed in reciprocal centimeters; ΔH_v is the latent heat of vaporization (cal mole^{-1}) at the normal boiling point temperature T_B (K); h is Planck's constant and R is the universal gas constant.

Equation (1) and Fig. 1 show that the general parabolic curve tends to a constant value: $Y_{x\to 0} = \ln(\Delta H_v/RT_B) \simeq 2.478$, when $X = \ln(hc\omega/kT_B) \to 0$. Comparing this (axial intercept) obtained dimensionless entropy value with the conventional Trouton constant[6], $S_{vap} = 19.5 \pm 2.1$ e.u.; or as rewritten in our Y-coordinate form, $Y_{\text{Trouton}} \cong 2.2837 \pm 0.1023$, we see that $Y_{x\to 0} > Y_{\text{Trouton}}$. This difference is not large and is possibly effectively caused by the anomalous vaporization behavior of metals (Fig. 1, Table 1). This in turn may be caused by the inherent nature of the metallic bond as well as the possible dimerization of metals in the vapor state, and the experimental difficulties present in obtaining correct vapor pressure and heat of vaporization values for metals[7].

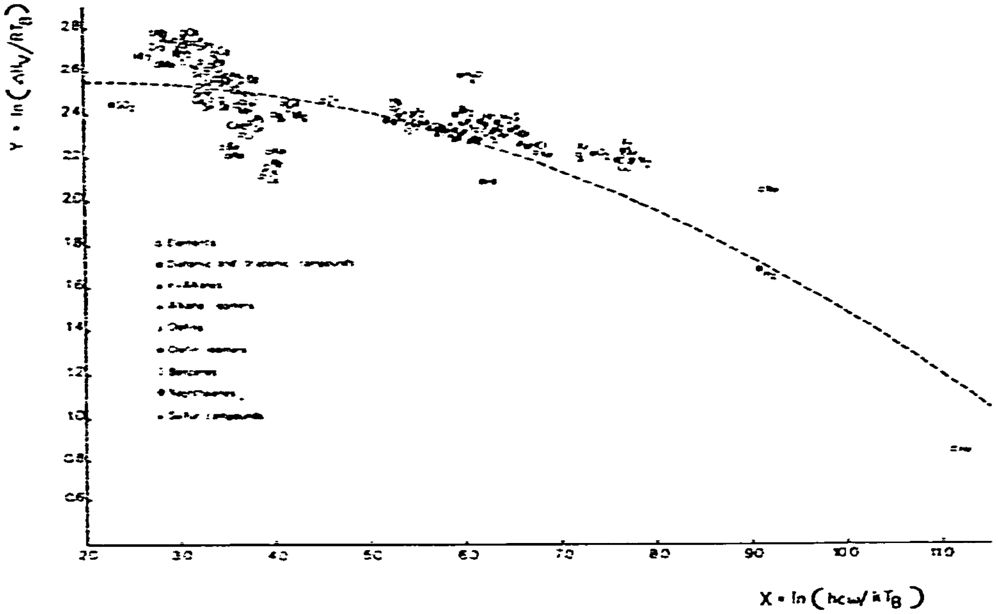

Fig. 1. Relation between the latent heat of vaporization and the first ionization potential for a series of liquids. The dashed curve was obtained by means of eqn (1).

TABLE 1

CALCULATED VALUES OF $X = \ln(hc\omega/kT_B)$ AND $Y = \ln(\Delta H_v/RT_B)$ FOR ELEMENTS

Element	*Parameter X*	*Parameter Y*	*First*[a] *ionization potential I.P., e.v.* $= \omega$ *(cm*$^{-1}$*)*	*Normal*[b] *boiling point,* T_B *(K)*	*Heat*[b] *of vaporization* ΔH_v *(cal mole*$^{-1}$*) at* T_B
He	11.1196	0.8411	24.481	4.21	19.4
Li	3.6568	2.3079	5.392	1615.35	32271
Be	3.6720	2.5559	9.32	2750	70400
B	3.1321	2.7365	8.296	4200	128800
Ne	9.1304	2.0396	21.559	27.1	414
Na	3.9441	2.2332	5.139	1155.15	21416
Mg	4.1647	2.4188	7.644	1378	30757
Al	3.2206	2.5361	5.984	2773	69603
Ar	7.6476	2.1951	15.759	87.27	1557.5
K	3.8869	2.1379	4.341	1033.15	17414
Ca	3.6934	2.3442	6.111	1765	35840
Sc	3.3178	2.5901	6.54	2750	72850
Ti	3.1043	2.6762	6.82	3550	102500
V	3.0648	2.7154	6.74	3650	109600
Cr	3.2802	2.6202	6.764	2953	80617
Mn	3.6141	2.4365	7.432	2324	52802
Fe	3.3076	2.5119	7.87	3343	81904
Co	3.3658	2.6811	7.86	3150	91400
Ni	3.2295	2.6525	6.88	3160	89112
Cu	3.4469	2.5480	7.726	2855	72717
Zn	4.5257	2.4592	9.391	1180	27424
Ga	3.3177	2.5037	6.0	2523	61309
Ge	3.3843	2.5626	7.88	3100	79900
Kr	7.2121	2.2044	13.996	119.8	2158
Rb	3.9191	2.1585	4.18	963.35	16575
Sr	3.6958	2.3445	5.692	1640	33240
Zr	2.8373	2.7109	6.84	4650	139000
Nb	2.7314	2.7796	6.88	5200	166500
Mo	2.7823	2.6399	7.10	5100	142000
Ru	2.9703	2.7460	7.364	4383	135700
Rh	3.0747	2.7010	7.46	4000	118400
Pd	3.3475	2.6328	8.33	3400	94000
Ag	3.5707	2.5058	7.574	2473	60218
Cd	4.6104	2.4488	8.991	1038	23874
In	3.3651	2.4625	5.785	2320	54100
Sn	3.3598	2.4680	7.342	2960	69400
Sb	3.9617	2.4660	8.639	1908	44648
Xe	6.7484	2.2200	12.127	165.05	3020
Cs	3.8692	2.1265	3.89	942.35	15702
Ba	3.4549	2.2516	5.21	1910	36070

(Continued on p. 358)

TABLE 1 (*continued*)

Element	*Parameter* X	*Parameter* Y	*First*[a] *ionization potential* $I.P.$, *e.v.* $= \omega\ (cm^{-1})$	*Normal*[b] *boiling point*, $T_B\ (K)$	*Heat*[b] *of vaporization* ΔH_v (*cal mole*$^{-1}$) *at* T_B
Hf	2.6926	2.6711	7.0	5500	158000
Os	3.0497	2.7821	8.5	4673	150000
Ir	3.1670	2.7347	9.0	4400	134700
Pt	3.2377	2.7063	9.0	4100	122000
Au	3.5025	2.5480	9.22	3223	81865
Hg	5.2581	2.4237	10.43	630	14131
Tl	3.6954	2.4531	6.106	1760	40656
Pb	3.7492	2.3668	7.41	2024	42889
Bi	4.0038	2.3997	7.287	1953	42771
Rn	6.3811	2.3329	10.746	211.15	4325
Ra	3.5270	2.2129	5.277	1800	32700

[a] All first ionization potential values listed are taken from ref. 13. [b] Normal boiling point and heat of vaporization values at the normal boiling point are taken from the following sources: (i) for elements He, Ne, Ar, Kr, Xe, Rn from ref. 14; (ii) for elements Cs, Rb, K, Na, Li from ref. 15; (iii) for elements Be, Ca, Sr, Ba, Ra, B, Ge, Sn, Sc, Ti, Zr, Hf, V, Hg, Nb, Mo, Co, Ru, Rh, Pd, Os, Ir, Pt from ref. 16; (iv) for elements Ag, Al, Au, Bi, Cd, Cr, Fe, Ga, Mg, Mn, Ni, Sb, Tl, Zn from ref. 17; (v) for elements Cu, Pb from ref. 18.

On the other hand, hydrocarbons although falling at their given X-values within the range of the Trouton constant limits (Fig. 1, Tables 1–4), introduce additional complexity. Hydrocarbons of which most notably n-alkanes and 1-olefins seem to follow a nearly straight line pattern up to their given carbon numbers (C_{17} for n-alkanes and C_{10} for 1-olefins). If we increase the carbon number n in any of these series, the question arises, will this extended homologous series follow the already established parabolic equation, or will these compound series form their own largely deviating curves? Letting $n \to \infty$, and comparing the simultaneous behavior of parameters defining the X and Y coordinates, we note that experimental $\Delta T_B \to 0$ as well as $\Delta\omega \to 0$ for these given series (Tables 2–4). If boiling points and ionization potentials approach a constant value as $n \to \infty$, we feel that Y–X lines for hydrocarbons should correspondingly curve even if entropy is an extensive property. This curving, however, may be somewhat slowed by an eventual increase in the configurational entropy since molecule chains become longer as $n \to \infty$. From these very brief considerations it appears that the calculated intercept, $Y_{x \to 0} = 2.478$, may prove to be indeed a fair average estimate for this type of generalization.

The introduction of the first ionization potential as a common denominator to describe the evaporation process for all compounds (ionic, metallic, covalent bonds) has made it possible to correlate the required energy for bond disruption in liquid

TABLE 2

CALCULATED VALUES OF $X = \ln(hc\omega/kT_B)$ AND $Y = \ln(\Delta H_v/RT_B)$ FOR n-ALKANES, n-ALKANE ISOMERS AND CYCLOPARAFFINS

Compound	*Parameter* X	*Parameter* Y	*First*[a] *ionization potential, I.P., e.v.* $= \omega$ (cm^{-1})	*Normal*[b] *boiling point,* T_B (K) *at* $p =$ *760 mm Hg*	*Heat*[b] *of vaporization* ΔH_v (*cal mole*$^{-1}$) *at* $p = 760$ *mm Hg*
Methane	7.2088	2.1760	13.0	111.65	1955
Ethane	6.5931	2.2607	11.65	184.55	3517
Propane	6.3217	2.2796	11.08	231.05	4487
n-Butane	6.1146	2.2902	10.63	272.67	5352
n-Pentane	5.9603	2.3051	10.33	309.19	6160
n-Hexane	5.8441	2.3175	10.17	341.89	6896
n-Heptane	5.7500	2.3282	10.06	371.58	7576
n-Octane	5.6762	2.3397	10.03	398.83	8225
n-Nonane	5.6141	2.3487	10.02	423.97	8823
n-Decane	5.5535	2.3572	9.95	447.3	9388
n-Undecane	5.5040	2.3648	9.93	469.08	9920
n-Dodecane	5.4614	2.3724	9.93	489.47	10430
n-Tridecane	5.4220	2.3790	9.92	508.62	10910
n-Tetradecane	5.3870	2.3862	9.92	526.73	11380
n-Pentadecane	5.3541	2.3922	9.91	543.84	11820
n-Hexadecane	5.3248	2.3978	9.91	560.01	12240
n-Heptadecane	5.2960	2.4032	9.89	575.17	12640

Compound	*Parameter* X	*Parameter* Y	*First*[c] *ionization potential, I.P., e.v.* $= \omega$ (cm^{-1})	*Normal*[b] *boiling point,* T_B (K) *at* $p =$ *760 mm Hg*	*Heat*[b] *of vaporization* ΔH_v (*cal mole*$^{-1}$) *at* $p = 760$ *mm Hg*
i-Butane	6.1515	2.2826	10.57	261.32	5090
i-Pentane	5.9827	2.2856	10.32	302.03	5901
2,2-Dimethylpropane	6.0520	2.2703	10.35	282.63	5438
2-Methylpentane	5.8643	2.3052	10.12	333.42	6643
3-Methylpentane	5.8513	2.3064	10.08	336.43	6711
2,2-Dimethylbutane	5.8904	2.2822	10.06	322.89	6287
2,3-Dimethylbutane	5.8612	2.2932	10.02	331.14	6519
2,2,4-Trimethylpentane	5.7277	2.3041	9.86	372.39	7411
Cyclopentane	5.9376	2.3207	10.53	322.41	6524
Cyclohexane	5.7807	2.3206	9.88	353.88	7160
Methylcyclohexane	5.7222	2.3034	9.85	374.08	7440

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[a] See ref. 19. [b] See ref. 20. [c] See ref. 21.

TABLE 3

CALCULATED VALUES OF $X = \ln(hc\omega/kT_B)$ AND $Y = \ln(\Delta H_v/RT_B)$ FOR AROMATIC, DIATOMIC AND TRIATOMIC SUBSTANCES

Compound	*Parameter X*	*Parameter Y*	*First*[a] *ionization potential, I.P., e.v.*	*Normal*[b] *boiling point, T_B (K)*	*Heat*[b] *of vaporization ΔH_v (cal mole^{-1}) at T_B*
Benzene	5.7166	2.3488	9.25	353.25	7352
Toluene	5.6063	2.3417	9.0	383.78	7931
o-Xylene	5.4940	2.3616	8.75	417.46	8800
m-Xylene	5.5066	2.3616	8.75	412.25	8690
p-Xylene	5.4911	2.3530	8.6	411.50	8600
1,2,3-Trimethylbenzene	5.4034	2.3721	8.6	449.23	9570
1,2,4-Trimethylbenzene	5.4068	2.3672	8.5	442.5	9380
1,3,5-Trimethylbenzene	5.4348	2.3723	8.65	437.87	9330
1,2,3,5-Tetramethylbenzene	5.3202	2.4143	8.3	471.20	10470
Ethylbenzene	5.5149	2.3466	8.76	409.33	8500
n-Propylbenzene	5.4555	2.3644	8.72	432.37	9140
1-Propylbenzene	5.4680	2.3616	8.69	425.54	8970
n-Butylbenzene	5.3979	2.3361	8.69	456.46	9380
s-Butylbenzene	5.4188	2.3246	8.68	446.49	9070
t-Butylbenzene	5.4282	2.3252	8.68	442.30	8990
Naphthalene	5.2569	2.3604	8.12	491.09	10340
1-Methylnaphthalene	5.1839	2.3693	7.96	517.84	11000
2-Methylnaphthalene	5.1904	2.3763	7.955	514.2	11000

Compound	*Parameter X*	*Parameter Y*	*First*[a] *ionization potential, I.P., e.v.*	*Normal*[c] *boiling point, T_B (K)*	*Heat*[c] *of vaporization ΔH_v (cal mole^{-1}) at T_B*
H_2	9.0802	1.6739	15.426	20.268	214.8
N_2	7.7572	2.1746	15.580	77.32	1352
O_2	7.3488	2.2080	12.075	90.15	1629.741
CO	7.5970	2.1865	14.01	81.61	1444.0
I_2	7.6696	2.2238	15.7	85.05	1562.582
Cl_2	6.3229	2.3288	11.48	239.11	4877.99
Br_2	5.9106	2.3878	10.55	331.85	7170.0
I_2	5.4647	2.3981	9.28	455.95	9968.69
HF	6.1850	2.0855	15.77	377	6030
HCl	6.6622	2.2428	12.74	189	3538
HBr	6.4865	2.3206	11.62	205.5	4158
HI	6.2293	2.3503	10.38	237.4	4948
H_2O	5.9701	2.5729	12.59	373.15	9717
H_2S	6.3461	2.3565	10.46	212.8	4463
CS_2	5.9036	2.3252	10.08	319.3	6490
SO_2	6.2996	2.4336	12.34	263.08	5960

[a] The ionization potential values for the first 9 substituted benzenes (including benzene) were taken from ref. 22; the remaining I.P. values from ref. 21. [b] See ref. 20. [c] All values from ref. 23, except value for H_2 (ref. 24) and H_2O (ref. 20).

TABLE 4

CALCULATED VALUES OF $X = \ln(hc\omega/kT_B)$ AND $Y = \ln(\Delta H_v/RT_B)$ FOR OLEFINS AND SULPHUR CONTAINING SUBSTANCES

Compound	*Parameter X*	*Parameter Y*	*First*[a] *ionization potential, I.P., e.v.*	*Normal*[b] *boiling point, T_B (K)*	*Heat*[b] *of vaporization ΔH_v (cal mole^{-1}) at T_B*
Ethane	6.5894	2.2632	10.62	169.44	3237
Propene	6.2275	2.2850	9.84	225.45	4402
1-Butene	6.0506	2.2901	9.76	266.89	5238
1-Pentene	5.9130	2.3023	9.66	303.12	6022
1-Hexene	5.8009	2.3130	9.59	336.64	6760
1-Heptene	5.7103	2.3218	9.54	366.79	7430
1-Octene	5.6351	2.3317	9.52	394.43	8070
1-Decene	5.5163	2.3494	9.51	443.72	9240
trans-2-Hexene	5.7421	2.3220	9.16	341.03	6910
trans-3-Hexene	5.7400	2.3258	9.12	340.24	6920
2-Ethyl-1-butene	5.7569	2.3271	9.21	337.83	6880
2,3-Dimethyl-2-butene	5.6544	2.3304	8.53	346.66	7083
2-Methyl-1-butene	5.8516	2.3103	9.12	304.31	6094
2-Methylpropene	6.0004	2.3017	9.26	266.25	5286
2-Butene (*cis*)	5.9699	2.3167	9.34	276.87	5580
2-Butene (*trans*)	5.9727	2.3014	9.27	274.03	5439
2-Methyl-2-butene	5.8020	2.3174	8.89	311.72	6287
1,3-Butadiene	5.9704	2.3174	9.07	268.74	5420
Acetylene	6.5511	2.3307	11.41	189.15	4050
Propyne	6.1759	2.3659	10.36	249.94	5290
1-Butyne	6.0404	2.3686	10.18	281.23	5970
3-Methyl-1-butene	5.9301	2.2893	9.51	293.21	5750

Compound	*Parameter X*	*Parameter Y*	*First*[c] *ionization potential, I.P., e.v.*	*Normal*[b] *boiling point, T_B (K)*	*Heat*[b] *of vaporization ΔH_v (cal mole^{-1}) at T_B*
Methanethiol	5.9725	2.3596	9.44	279.11	5872
Ethanethiol	5.8570	2.3469	9.285	308.15	6401
1-Propanethiol	5.7463	2.3438	9.195	340.87	7059
1-Butanethiol	5.6540	2.3446	9.14	371.61	7702
Dimethylsulfide	5.7827	2.3447	8.685	310.48	6435
Ethylmethylsulfide	5.6768	2.3464	8.55	339.8	7055
Diethylsulfide	5.7529	2.3474	8.430	365.25	7591
Di-n-propylsulfide	5.4448	2.3606	8.30	415.99	8760
Benzenethiol	5.3871	2.4012	8.33	442.29	9700

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[a] All I.P. values from ref. 25, except those of 2-methyl-1-butene; 1,3-butadiene; acetylene; propyne; 1-butyne; 3-methyl-1-butene (ref. 21). [b] See ref. 20. [c] See ref. 21.

(latent heat of vaporization) to the molecular exchange forces. So we have renewedly[8–12] implied that it may be possible to consider the evaporation mechanism on the basis of the thermally excited vibrational state of the molecule in terms of the quantum-mechanical theory of intermolecular force interaction in the liquid state.

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