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Internal Pressure and Related Physical Properties

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INTERNAL PRESSURE

AND

RELATED PHYSICAL PROPERTIES

By

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PREFACE

What is internal pressure? That question has never been answered in a satisfactory manner. Probably the best answer is the simple statement that it is a measure of the attraction between molecules. While this is true it gives no indication of what causes the attractive force or of the effects which this attraction has on a substance.

In this thesis an attempt will be made to use this vague definition of internal pressure to find a method of calculating internal pressure using data for various physical properties. The liquid state of various substances will be considered. A relationship which holds in the liquid state should hold in the solid or gaseous state with some possible modifications taking into account the energy absorbed or given off as a substance changes from one state to another.

I wish to thank Dr. Scott L. Kittsley of the Chemistry Department of Marquette University for the many helpful suggestions which he provided during the course of the work on this thesis. Beyond this, he provided the original suggestion that this work be undertaken.

TABLE OF CONTENTS

I. INTRODUCTION

Boyle's law, which states that at constant temperature the volume of a definite mass of gas is inversely proportional to the pressure (2), is obeyed only within certain temperature ranges. According to this law the product of pressure times volume should be a constant. Actually as the pressure is varied the value of the product PV varies. It has been shown the more liquifiable gases show the greatest deviations from this law. (2)

Charles' law may be expressed most simply in the following manner: at constant pressure, the volume of a gas expands by the same fraction of its volume at 0°C for every one degree rise in temperature. (2) Mathematically expressed this is:

$$V_t = V_o(1 + \alpha t)$$

V_t = volume at t°C

V_o = volume at 0°C

α = coefficient of cubical expansion

Then, according to Charles' law, α should be the same for all gases. Accurate measurements to determine the value of α show that this is not true. Again it is the most easily liquified gases which show the greatest deviations. At very low pressures α does approach a constant value. (2)

Avogadro's law holds that equal volumes of all gases

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(2) Glasstone, S., Textbook of Physical Chemistry, 2nd Ed., New York, D. Van Nostrand Co., (1946) 191.

(2) Glasstone, S., Ibid., 245.

(2) Glasstone, S., Ibid., 191.

(2) Glasstone, S., Ibid., 247.

under the same conditions of temperature and pressure contain equal numbers of molecules. (2) This law is not obeyed exactly either and the largest deviations, as before, are shown by the more easily liquified gases.

The laws mentioned are applicable only to an ideal gas which has no molecular attraction and which is in a perfect state of randomness. In fact, it is the interaction of molecules which is partly responsible for gaseous behavior deviating from ideality as defined by the laws of Charles, Boyle, and Avogadro. This attraction between molecules may also be used as an explanation of the various states of matter. Since liquids have a more definite shape than gases and have a surface, the cohesive forces between molecules must be greater than in the gaseous state. Further, solids must have an even greater molecular attraction since they possess a definite shape and surfaces. Since the states of matter vary with temperature it may be stated with certainty that the molecular attraction depends on the absolute temperature of the system under consideration. Also, the lower the temperature of the system the higher the molecular attraction and the higher the temperature the lower the molecular attraction.

Molecular attraction is of most interest concerning liquids and solids. Since gases under ordinary conditions follow rather closely the laws for a perfect gas the molecular attraction must be slight in most cases. In liquids, however, this

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(2) Glasstone, S., Textbook of Physical Chemistry, 2nd Ed., New York, D. Van Nostrand Co., (1946) 248.

is not true and molecular attraction becomes a very important factor.

The familiar equation of van der Waals was one of the first attempts to take into account the deviations from ideal behavior caused by molecular attraction. The derivation of this equation may be stated in fairly simple terms. A molecule in the interior of a gas has equal forces exerted on it in all directions. As this molecule approaches one of the walls of the retaining vessel this condition changes and a force is exerted which tends to pull the molecule toward the center of the gas. Because of this force the measured pressure P is less than that which should be exerted according to the kinetic theory. The ideal pressure is then equal to $P + P_a$, where P_a is a correction term. Since the force exerted on a molecule near the wall is proportional to the number of molecules it is also proportional to the density of the gas. The number of molecules approaching the wall will also be proportional to the density of the gas so the total attractive force is proportional to the density squared. The density is inversely proportional to the volume of one mole of the gas and therefore:

$$P_a \propto d^2 \propto \frac{1}{V^2}$$

and

$$P + P_a = P + \frac{a}{V^2}$$

where a is a proportionality factor.

The term $\frac{a}{V^2}$ is a measure of the attractive force of the molecules. Since it is combined with the pressure term in the ideal gas equation it is called the cohesion pressure or internal pressure. (2) It was shown earlier that the most easily liquified gases have the highest internal pressures and therefore these gases must have the highest values for the constant a. Since van der Waals equation is empirical and not exact the term $\frac{a}{V^2}$ will not give a true value of the molecular attraction.

Van der Waals derived his equation in 1873 and since that time others have continually tried to determine accurately the internal pressure of different substances. Amagat (1), through a study of van der Waals' equation, determined that the attraction between molecules varies inversely as the fourth power of the distance between the molecules.

W. C. Mc Clewis (13) by studying heats of vaporization and expansion came to the conclusion that since these heats are of the same order of magnitude the range of attraction between molecules must be very small. It should be about the same order as the mean distance between molecules or about 10^{-8} cm. Shortly after this he stated that the attraction between molecules is electromagnetic and not electrostatic as had been held. In order to follow up on this he attempted to relate internal pressure to the dielectric constant and permeability of substances. His observation was that substances

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(2) Glasstone, S., <u>Textbook of Physical Chemistry</u>, 2nd Ed., New York, D. Van Nostrand Co., (1946) 289.

(1) Amagat, E. H., <u>Ann. chim. phys.</u>, <u>28</u>, 5-48 (1883).

(13) Mc Clewis, W. C., <u>Phil. Mag.</u>, <u>25</u>, 61-65 (1888).

having the larger internal pressures have the smaller permeability. Related to this was the fact that a rise in temperature which partially destroys the orientation of molecules alters the inverse ratio of molecular distance to internal pressure from the fourth to the third power. (14) Mc Clewis (15) was finally led to the conclusion that internal pressures could not be calculated except through some new assumption concerning internal pressure or the change of internal pressure with respect to temperature.

A. Leduc (10), another of the pioneer workers in the field, started from van der Waals' equation and said that the internal pressure of any gas at constant temperature is inversely proportional to the square of the specific volume. Later he stated that for gases of the same molecular constitution and at a corresponding temperature state the attraction between molecules of a gas is proportional to the square of the mass of the molecules and inversely proportional to the fourth power of their distance apart. (11) Leduc's statement concerning the effect of temperature on internal pressure appears to be another attempt to explain the deviation of gases from the gas laws. This statement is that the internal pressure approaches a finite limit as the temperature increases indefinitely and that this limit is not zero. (12) This statement has been opposed and contradicted by the state-

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(14) Mc Clewis, W. C., <u>Phil</u>. <u>Mag</u>., <u>28</u>, 104-16 (1889).
(15) Mc Clewis, W. C., <u>Trans</u>. <u>Faraday Soc</u>., <u>7</u>, 94-115 (1911).
(10) Leduc, A., <u>Compt</u>. <u>rend</u>., <u>148</u>, 1391-4 (1909).
(11) Leduc, A., <u>Compt</u>. <u>rend</u>., <u>153</u>, 179-82 (1911).
(12) Leduc, A., <u>Compt</u>. <u>rend</u>., <u>161</u>, 97-100 (1915).

ment that the internal pressure holds liquids together and vanishes at the critical point. (3)

The object of this thesis is to find some relationship between the internal pressure of a liquid and physical properties of that liquid. Hildebrand (6) has shown that relative values of internal pressure can be calculated using the ratio:

$$\frac{E_s}{V^{1/3}}$$

where

E_s = surface energy
V = molal volume

From this, by taking any arbitrary standard of one, the ratio of the internal pressure of other liquids to this standard may be found. The internal pressure of naphthalene is approximately 3600 atm. (2) and is often used as the standard for comparison. For this thesis benzene will be taken as the standard. If a relationship between physical properties and these relative values can be found it should be possible to calculate the internal pressures from these same properties.

Since surface tension is caused by an uneven molecular attraction toward surface molecules a great deal of work has been done in attempting to calculate internal pressures from surface tension date. By using surface tension data Walden (18)

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(3) Hallstrom, M. of, <u>Ann</u>. <u>Acad</u>. <u>Sci</u>. <u>Fennice</u>, Ser. A. II, No. 5, 30 (1942).
(6) Hildebrand, J. H., <u>J</u>. <u>Am</u>. <u>Chem</u>. <u>Soc</u>., <u>43</u>, 500-507 (1921).
(2) Glasstone, S., <u>Textbook</u> <u>of</u> <u>Physical</u> <u>Chemistry</u>, 2nd Ed., New York, D. Van Nostrand Co., (1946) 480.
(18) Walden, P., <u>Ion</u>, <u>I</u>, 402-12.

had previously arrived at the same relationship as Hildebrand. He expressed it in a different form, however. He stated that the diameter of the molecules of a liquid was proportional to:

$$\frac{E_o}{K}$$

where

E_o = surface energy
K = internal pressure

He also set up another empirical equation using values of the van der Waals constants at the critical point. This expression is: (19)

$$\frac{K}{\pi} = 34.2$$

where

K = internal pressure
π = critical pressure

In a similar manner using van der Waals constants at the critical point Stakhorskii (17) showed that:

$$P_i = \frac{4.35(l)}{v}$$

where

P_i = internal pressure
l = latent heat of vaporization
v = specific volume

He also set up one of the very few empirical equations for internal pressure which included only the surface tension of the liquid in question: (16)

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(19) Walden, P., Z. Physik. Chem., 66, 385-444 (1909).
(17) Stakhorskii, K. M., J. Russ. Phys. Chem. Soc., 58, 966-82 (1926).
(16) Stakhorskii, K., Urkrainskii Khem. Zhurnal, 1, 544-52 (1925).

$$P_i = 77.75\gamma$$

where

γ = surface tension

The heat of vaporization of a liquid has been used in several empirical equations for determining internal pressures. Using Stephan's assumption that the work required to bring a molecule to the surface of a liquid is one-half that for the vaporization, Hildebrand (5) set up the following expression:

$$\pi = 20.65 \frac{(L - RT)}{V}$$

where

π = internal pressure
L = heat of vaporization
V = molecular volume
T = boiling point

Assuming that the internal molar latent heat of vaporization is a measure of the work done against the internal pressure in one mole of a liquid occupying a volume V

$$\left(\frac{\partial E}{\partial V}\right)_v V \approx L_i$$

where

E = change of internal energy
V = change of volume
V = volume occupied
L_i = internal molar latent heat of vaporization

Internal pressure is equal to $\left(\frac{\partial E}{\partial V}\right)_T$ since this gives the deviation from ideal behavior. Therefore:

$$P_i = \left(\frac{\partial E}{\partial V}\right)_T \approx \frac{L_i}{V}$$

where

P_i = internal pressure

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(5) Hildebrand, J. H., J. Am. Chem. Soc., 41, 1067-1080 (1919).

Hildebrand (2) has shown that L_i is approximately equal to:

$$-1400 + 24.5T_b$$

where T_b is the normal boiling point on the absolute scale.

By far the most exact expressions for internal pressure can be obtained from wave and quantum mechanics. The attractions of permanent dipoles were at one time considered to be the cause of molecular attraction. Since the magnitude of any attraction or repulsion depends on the orientation of the dipoles, this has been called the orientation effect. If all orientations were possible this effect would be zero but it has been shown statistically that certain orientations are preferred. The mean interaction potential energy between two dipolar molecules is given by: (2)

$$U_o = -\frac{2u^4}{3r^6kT}$$

where

u = dipole moment
r = distance between molecules
g = Boltzmann gas constant

The negative sign shows that work has to be done on the molecules to separate them.

Any dipole will induce a dipole in nearby molecules and a further attraction will result. This effect is independent of temperature: (2)

$$U_r = -2\alpha\frac{u^2}{r^6}$$

where

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(2) Glasstone, S., <u>Textbook</u> <u>of</u> <u>Physical</u> <u>Chemistry</u>, 2nd Ed., New York, D. Van Nostrand Co., (1946) 480.
(2) Glasstone, S., <u>Ibid</u>., 298.
(2) Glasstone, S., <u>Ibid</u>., 299.

α = polarizability of molecule
u = dipole moment
r = distance between molecules

These equations meet with two objections:

1. The equations are applicable to molecular pairs but are not additive.
2. Many molecules which do not have permanent dipoles show large attractions.

London solved these difficulties by using the methods of quantum mechanics. According to quantum mechanics all molecules possess energy even at their lowest state and therefore show some vibrations between the nucleus and the electrons. The different arrangements of the nucleus and electrons will set up dipole moments in the molecule. These dipoles will induce dipoles in nearby molecules and result in a net attraction between the molecules. The interaction energy from this effect is: (2)

$$U_D = -\frac{3}{4}\frac{hv_0\alpha^2}{r^6}$$

where

h = Planck's constant
v_0 = characteristic frequency of the molecule
α = polarizability of the molecule
r = distance between molecules

The forces are said to be due to the dispersion effect because the oscillations producing the attractive forces are responsible for the dispersion of light by molecules. This dispersion effect is responsible for the greatest part of

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(2) Glasstone, S., Textbook of Physical Chemistry, 2nd Ed., New York, D. Van Nostrand Co., (1946) 299.

the attractive force in most molecules. When a large permanent dipole is present in a molecule the orientation effect becomes fairly large. The induction effect is never very large. The equations shown give the potential energy of interaction. The attractive force is found by differentiation with respect to r. It is therefore proportional to r^{-7}.

An exact expression must include a factor for the repulsion of the molecules. (2) The total attraction energy of molecules may be represented by:

$$U = Ar^{-6} + Br^{-12}$$

where

r = distance between molecules
A & B = constants

The first term represents the attractive energy and the second term represents the repulsive energy. Ar^{-6} is almost identical with the dispersion effect for simple molecules and therefore A is equal to $-\frac{3}{4} h v_o \alpha^2$

where

v_o = characteristic frequency of the molecule
h = Planck's constant
α = polarizability of the molecule

Hildebrand (4) has done a vast amount of work on the prediction of solubilities through internal pressures. Raoult's law can be used to predict solubilities for non-polar liquids having equal internal pressures. Non-polar liquids with different internal pressures give positive deviations from Raoult's

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(2) Glasstone, S., <u>Textbook of Physical Chemistry</u>, 2nd Ed., New York, D. Van Nostrand Co., (1946) 300.
(4) Hildebrand, J. H., <u>J. Am. Chem. Soc.</u>, <u>38</u>, 1452 (1916).

law and show a solubility less than that predicted from the internal pressures. A solubility equation has been developed, one form of which may be written as follows: (7)

$$4.576T\log\frac{(a_2)}{x_2} = v_2\,\phi^2(\delta_1 - \delta_2)^2$$

where

a_2 = activity of solute
x_2 = mole fraction of solute
v_2 = molar volume of the supercooled liquid solute
ϕ = volume fraction of solvent
δ = solubility parameter
= $\left(\frac{\Delta E}{V}\right)^{\frac{1}{2}}$
E = molar energy of vaporization
V = molar volume of pure component in liquid state

δ is a measure of the internal pressure and therefore solubility is dependent on internal pressure.

Hildebrand (8) has come to the conclusion that solubility is increased by differences in molal volume and diminished by differences in internal pressure. The former causes deviations from ideal entropy, the latter from ideal (zero) heat of mixing of the pure liquid components.

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(7) Hildebrand, J. H., Benesi, A. H., and Mower, L. M., J. Am. Chem. Soc., 72, 1017-20 (1950).
(8) Hildebrand, J. H., and Gjaldbaek, J. Am. Chem. Soc., 72, 609-11 (1950).

II. RESULTS

The results given in the following tables are tabulated according to the equation by which they were calculated. All calculations were made for corresponding states of temperature based on benzene. The states of benzene used as a basis for calculations were from 20°C to 30°C and from 40°C to 50°C. The values used in the calculations were taken from the International Critical Tables. (9) Various values of surface tension and viscosity were interpolated to the proper temperature since the values at the corresponding temperature states were not given. The literature values cited as a comparison with calculated results are based on benzene as a standard of one. (2)

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(9) International Critical Tables, New York, McGraw-Hill Book Co., Vol. IV, (1938), Vol. V, (1929), Vol. VII, (1930).

(2) Glasstone, S., Textbook of Physical Chemistry, 2nd Ed., New York, D. Van Nostrand Co., (1946) 480.

TABLE I

THE CORRESPONDING STATES USED IN CALCULATIONS

Compound	Critical Temp. (K)	Corresponding State % of T. of Benzene	Corresponding Temp. State	Temp. of Calc. (C)
Benzene	561.6	0.522-0.540	293.1-303.1	20-30
Carbon Tet.	556.25	0.522-0.540	290.3-300.4	17.3-27.3
Chloro-benzene	632.3	0.522-0.540	330-342	56.9-68.9
Hexane	507.9	0.522-0.540	265.4-274.3	-7.7-1.2
Ethyl Acetate	523.2	0.522-0.540	273-282	0.0-9
Carbon Disulfide	546.1	0.522-0.540	285.5-295	12.4-22
Water	647.1	0.522-0.540	338-350	65-77

Compound	Critical Temp. (K)	Corresponding State % of T. of Benzene	Corresponding Temp. State (K)	Temp. of Calc. (C)
Benzene	561.6	0.557-0.575	313.1-323.1	40-50
Carbon Tet.	556.25	0.557-0.575	310-320	37-47
Chloro-benzene	623.3	0.557-0.575	352-364	79-91
Hexane	507.9	0.557-0.575	283-292	10-19
Ethyl Acetate	523.2	0.557-0.575	291.5-300.5	18.4-27.4
Carbon Disulfide	546.1	0.557-0.575	304-314	31-41
Water	647.1	0.557-0.575	360.5-372	87.4-99

TABLE II

RESULTS USING EQUATION ONE

Compound	$\Delta\gamma$	Δn	X	$\frac{\text{Benzene}}{\text{X}}$	Literature Value (2)
Benzene	1.32	0.086	1.406		
Carbon Tet.	1.24	0.14	1.38	1.02	1.18
Chlorobenzene	1.37	0.053	1.423	0.987	1.0
Hexane	0.93	0.37	0.967	1.45	1.71
Ethyl Acetate	1.17	0.74	1.244	1.13	1.31
Carbon Disulfide	1.48	0.23	0.503	0.935	0.813

TABLE III

RESULTS USING EQUATION TWO

Compound	$\Delta\gamma$	Δn	ΔT	X	$\frac{\text{Benzene}}{\text{X}}$	Literature Value (2)
Benzene	1.32	0.086	10	.141		
Carbon Tet.	1.24	0.14	10	0.138	1.02	1.18
Chlorobenzene	1.37	0.053	12	0.119	1.18	1.0
Hexane	0.93	0.37	8.9	.109	1.285	1.71
Ethyl Acetate	1.17	0.74	9.0	.138	1.017	1.31
Carbon Disulfide	1.48	0.23	9.6	.156	.898	0.813

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(2) Glasstone, S., Textbook of Physical Chemistry, 2nd Ed., New York, D. Van Nostrand Co., (1946) 480.

TABLE IV

RESULTS USING EQUATION THREE

Compound	$\Delta\gamma$	Δn	ΔT	X	$\frac{\text{Benzene}}{\text{X}}$	Literature Value (2)
Benzene	1.32	0.086	10	6.78		
Chlorobenzene	1.37	0.053	12	7.58	0.895	1.0
Carbon Tet.	1.24	0.14	10	6.36	1.07	1.18
Hexane	0.93	0.37	8.9	7.72	0.878	1.71

TABLE V

RESULTS USING EQUATION FOUR

Compound	$\Delta\gamma$	Δn	ΔT	X	$\frac{\text{Benzene}}{\text{X}}$	Literature Value (2)
Benzene	1.32	0.086	10	8.805		
Chlorobenzene	1.37	0.053	12	9.75	0.904	1.0
Carbon Tet.	1.24	0.14	10	8.45	1.05	1.18
Hexane	0.93	0.37	8.9	9.97	0.884	1.71

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(2) Glasstone, S., Textbook of Physical Chemistry, 2nd Ed., New York, D. Van Nostrand Co., (1946) 480.

TABLE VI

RESULTS USING EQUATION FIVE

Compound	$\Delta\gamma$	$\Delta\eta$	ΔT	C	A
Benzene	1.32	0.086	10	1	7.51
Carbon Tet.	1.24	0.14	10	1.18	8.6
Chlorobenzene	1.37	0.053	12	1	8.7
Carbon Disulfide	1.48	0.23	9.6	0.813	5.3
Ethyl Acetate	1.17	0.74	9.0	1.31	10
Hexane	0.93	0.37	8.9	1.71	16.3

TABLE VII

RESULTS USING EQUATION SIX

Compound	Surface Tension (a)	Viscosity (a)	C	A	B
Carbon Tet.	27.04-25.9	1.011-.87	1.18	0.358	0.87
Chlorobenzene	28.84-27.5	0.499-.47	1.00	0.05	0.23
Ethyl Acetate	26.9-25.5	.588-.514	1.31	0.375	0.148
Water	65.3-62.05	.436-.328	0.211	0.026	0.41
Carbon Disulfide	33.45-32.6	.387-.364	0.815	0.212	0.0076

(a) The values given are those of the extremes of the corresponding temperature state.

TABLE VIII

RESULTS USING EQUATION SEVEN

Corresponding state - Benzene 20°C-30°C.

Compound	$\Delta \gamma$	Δn	ΔT	C	A	Dipole Moment
Benzene	1.32	0.086	10	1	1.40	0
Chlorobenzene	1.37	0.053	12	1	1.36	1.7
Carbon Tet.	1.24	0.14	10	1.18	1.25	0
Hexane	0.93	0.37	8.9	1.71	1.41	0
Carbon Disulfide	1.48	0.23	9.6	.813	2.19	0
Ethyl Acetate	1.17	0.74	9.0	1.31	1.36	1.9
Water	3.15	0.108	12	.211	1.48	1.84

TABLE IX

RESULTS USING EQUATION SEVEN

Corresponding state - Benzene 40°C-50°C.

Compound	$\Delta \gamma$	Δn	ΔT	C	A	Dipole Moment
Benzene	1.28	0.056	10	1	1.48	0
Chlorobenzene	1.33	0.0544	12	1	1.37	1.7
Carbon Tet.	1.2	0.011	10	1.18	1.31	0
Hexane	0.935	0.031	8.9	1.71	1.44	0
Carbon Disulfide	1.43	0.033	9.6	.813	1.81	0
Ethyl Acetate	1.17	0.046	9.0	1.31	1.57	1.9
Water	1.79	0.049	12	.211	1.57	1.84

TABLE X

RESULTS USING EQUATION EIGHT

Corresponding state - Benzene 20°C-30°C.

Compound	$\Delta\gamma$	$\Delta\eta$	ΔT	C	A	Dipole Moment
Benzene	1.32	0.086	10	1	1.40	0
Chlorobenzene	1.37	0.053	12	1	1.36	1.7
Carbon Tet.	1.24	0.14	10	1	1.21	0
Hexane	0.93	0.37	8.9	1	1.28	0
Carbon Disulfide	1.48	0.23	9.6	1	2.24	0
Ethyl Acetate	1.17	0.74	9.0	1	1.29	1.9
Water	3.15	0.108	12	1	1.9	1.84

TABLE XI

RESULTS USING EQUATION EIGHT

Corresponding state - Benzene 40°C-50°C.

Compound	$\Delta\gamma$	$\Delta\eta$	ΔT	C	A	Dipole Moment
Benzene	1.28	0.056	10	1	1.48	0
Chlorobenzene	1.33	0.0544	12	1	1.37	1.7
Carbon Tet.	1.2	0.011	10	1	1.27	0
Hexane	0.935	0.031	8.9	1	1.3	0
Carbon Disulfide	1.43	0.033	9.6	1	1.81	0
Ethyl Acetate	1.17	0.046	9.0	1	1.5	1.9
Water	1.79	0.049	12	1	1.79	1.84

III. DISCUSSION

It was pointed out on page two that internal pressure is dependent on temperature; the internal pressure increases as the temperature decreases. In order to take this into account the calculations were made at corresponding states of temperature.

Two general types of equations were used to find a relationship between surface tension, viscosity, and internal pressure. Equations one through four are of the type:

$$f(\gamma) + f(\eta) = X$$

where

$f(\gamma)$ = a function of surface tension
$f(\eta)$ = a function of viscosity
X = a constant to which the given equation is equal

The value of X for benzene was divided by the value of X for the various compounds used in the calculations. These values were compared with the values obtained from the literature. The object of this procedure was to find some relationship from which the calculated ratios of internal pressures would be equal to the literature values.

Equations five through eight may be expressed in the general form:

$$A f(\gamma) + B f(\eta) = C$$

where

$f(\gamma)$ = a function of surface tension
$f(\eta)$ = a function of viscosity
A & B = empirical constants

C = the literature value of the internal pressure ratios based on benzene as one

The object of these equations was to find some relationship involving empirical constants which could be used to calculate the ratios of internal pressure.

The first equation is a summation of the change of viscosity and change of surface tension across the interval of the constant corresponding temperature state based on benzene from 20°C to 30°C. The equation is:

$$\Delta\gamma + \Delta_n = X$$

where

$\Delta\gamma$ = change of surface tension
Δ_n = change of viscosity
X = constant for each substance

The values of X for benzene divided by X for the other substances used show that this relationship does not give consistent results. The calculated result for chlorobenzene must be raised to a power slightly less than one to obtain the literature value while the other values must be raised to powers greater than two and the value for carbon tetrachloride must be raised to a very high power.

Equation two is a modification of equation one in which the change of surface tension and the change of viscosity in the proper temperature range are divided by the number of degrees in the temperature range. This gives the change of surface tension and viscosity per degree rise in temperature. This equation is:

$$\frac{\Delta\gamma}{\Delta T} + \frac{\Delta_n}{\Delta T} = X$$

where

$\Delta\gamma$ = change of surface tension
Δn = change of viscosity
ΔT = temperature range in corresponding state
X = a constant for each substance

The results of this equation show a greater variance from the literature values except for the case of carbon tetrachloride, which has the same temperature range as benzene in the corresponding state. The result for carbon tetrachloride is therefore the same as that obtained from equation number one.

Equation three is a further modification of equation one:

$$\ln\frac{\Delta\gamma}{\Delta T}+\ln\frac{\Delta n}{\Delta T}=X$$

where

$\Delta\gamma$ = change of surface tension
Δn = change of viscosity
ΔT = temperature range in corresponding state
X = a constant for each substance

Calculations using equation three show that the values of the ratios of internal pressure for chlorobenzene and for hexane are lowered considerably while the value for carbon tetrachloride is raised slightly. In order to obtain further information on this tendency another modification was made on the equation. This was done by multiplying the first term of the equation by two, giving equation four:

$$2\ln\frac{\Delta\gamma}{\Delta T}+\ln\frac{\Delta n}{\Delta T}=X$$

The various terms here being the same as in the previous equations.

The results obtained from this equation show a reversal of the trend noted with equation three. This reversal is such that it appears that an equation of this type will not provide a means of calculating the ratios of internal pressures from surface tension and viscosity date.

The second type of equation employs the known values of the ratios of the internal pressures and is solved for empirical constants.

Equation five is the first equation of this type:

$$A\frac{\Delta \gamma}{\Delta T} + \frac{\Delta \eta}{\Delta T} = C$$

where

$\Delta \gamma$ = change of surface tension
$\Delta \eta$ = change of viscosity
ΔT = temperature range in corresponding state
C = ratio of internal pressure to that of benzene
A = empirical constant

On page 20 the general equation was shown with two empirical constants. In this equation the value of B is taken as one. B is a multiplier of the second term in the equation.

The value of A calculated by this equation varies considerably. The value is close between carbon tetrachloride, benzene, and chlorobenzene. These three show the best agreement throughout. The surprising fact is that carbon tetrachloride is usually very close to one or the other while the third is somewhat different. Since benzene and chlorobenzene have the same internal pressures it would seem that they ought to be very close with carbon tetrachloride varying. (2)

Equation six uses the surface tension, and viscosity at the extremes of the temperature range of the corresponding state. Two empirical constants are solved for through simultaneous equations. The equation is:

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(2) Glasstone, S., Textbook of Physical Chemistry, 2nd Ed., New York, D. Van Nostrand Co., (1946) 480.

$$A \ln \gamma + B \ln n = C$$

where

γ = surface tension
n = viscosity
A & B = empirical constants
C = known ratio of internal pressures based on benzene as one

The values of A and B calculated from this equation agree in sign but not in magnitude. While the value of A varies considerably between different compounds it is positive in all cases. The same holds for B with the exception of the sign. B is negative in all cases.

Equation seven might be considered as a modification of equation five. The equation is:

$$A\left(\ln \frac{\Delta \gamma}{\Delta T}\right)^2 + \ln \frac{\Delta n}{\Delta T} = C$$

where

$\Delta \gamma$ = change of surface tension
Δn = change of viscosity
ΔT = temperature range of corresponding state
A = empirical constant
C = ratio of internal pressures based on benzene as one

The values of A calculated from this equation show a much better agreement except in the cases of carbon disulfide and water. This equation was used for calculations involving two corresponding temperature states. The agreement is seen to be fairly good in both temperature ranges. In the higher range the value of A for carbon disulfide is much closer to the average value in the temperature range. A comparison of the averages shows that by neglecting the value for carbon disulfide one average can be calculated from the other. Using carbon disulfide in the calculations the average for the temperature ranges based on benzene is as follows:

20°C-30°C	1.49
40°C-50°C	1.51
40°C-50°C (Calculated)	1.585

Neglecting carbon disulfide the averages are:

20°C-30°C	1.38
40°C-50°C	1.46
40°C-50°C (Calculated)	1.47

The calculation of the average was made with the following equation:

$$M_2 = \frac{X_2}{X_1} (M_1)$$

where

M_2 = average to be calculated

M_1 = average known

X_1 & X_2 = corresponding state as a fraction of the critical temperature

30°C is 0.54 of the critical temperature of benzene. 40°C is 0.575 of the critical temperature of benzene. The calculation of the average for the higher corresponding state neglecting carbon disulfide is then:

$$M_2 = \frac{0.575}{0.54} (1.38)$$

$$M_2 = 1.47$$

where M_2 is again the average to be calculated.

While this calculation works for the averages it does not hold for each individual value obtained. For example, the value of A for chlorobenzene increases from 1.36 to 1.37 while the calculated values are 1.36 to 1.45.

The dipole moment seems to have very little effect since carbon disulfide, which shows the greatest variance, has a moment of zero and water, which also varies considerably, has a moment of 1.84 electrostatic units. This is in agreement with the statement on page four that molecular attraction is electromagnetic and not electrostatic and with the quantum mechanical consideration on page ten. There it was stated that in most cases dipoles, both permanent and induced, generally contribute very little to molecular attraction.

Equation eight assumes that internal pressures are equal at corresponding temperature states. The equation is the same as equation seven except the ratio C is one in all cases. The values of A calculated by using this modification show that this is not true since there is a wide variance in the values. These results indicate the internal pressures of various substances are not equal at the boiling point. This being the case the effect of temperature on internal pressure must depend to a large extent on the size and structure of the molecules. Along this line it is seen that water and carbon disulfide, each of which have three atoms per molecule and the molecules of which are very small, show the greatest deviations from the general tendency of the results. This suggests an effect which may be analagous to steric hindrance. Since the compounds with larger molecules show a close agreement in equations seven and eight such an effect might be one explanation of the difficulties involved in attempting to calculate internal pressures. These results agree with what was stated on pages six and seven concerning molecular diameter and internal pressure.

IV. SUMMARY AND CONCLUSIONS

The equation: $$A\left(\ln \frac{\Delta\gamma}{\Delta T}\right)^2 + \ln \frac{\Delta\eta}{\Delta T} = C$$

where

$\Delta\gamma$ = change of surface tension

$\Delta\eta$ = change of viscosity

ΔT = temperature range of corresponding state

A = empirical constant

C = known ratio of internal pressure based on benzene as one

was solved for A. It was found that by neglecting the value for carbon disulfide the average value of A in one corresponding temperature state could be calculated from the value in another corresponding temperature state. The individual values cannot be calculated in this manner, however.

The dipole moment was shown to have very little effect on internal pressure. Along with this, the compounds showing the greatest variations appeared to be those with the smallest molecules. This leads to the conclusion that a factor analagous to steric hindrance may enter the picture. This would account for the relative agreement of the value of A calculated for compounds having larger molecules.

V. SUGGESTIONS FOR FURTHER STUDY

The major point which presents itself for further work is the effect of molecular diameter and volume on the value of A calculated from equation seven. This is a large problem in itself since very little data is available on molecular diameters and volumes. It might be helpful to determine the effect of apparent molecular volumes. This should give some indication of the effects of molecular size on internal pressure.

Equation seven could probably be made more exact by employing data on more physical properties. The main objection to this is that the equation would become very unwieldy. At the same time the temperature ranges of the corresponding states ought to be made smaller in order to determine the effect of temperature on internal pressure. From what has been noted concerning the failure of the equation to hold on the assumption that internal pressures are equal at corresponding temperature states, temperature effects must depend upon molecular size and complexity. Therefore, it appears that molecular diameter, volume, and temperature ought to be studied together.

VI. ANNOTATED BIBLIOGRAPHY

(1) Amagat, E. H., "Internal Pressure in Fluids", *Ann. chim. phys.*, *28*, 5-48 (1883).

Amagat's work provided some information concerning the nature and magnitude of internal pressure.

(2) Glasstone, S., *Textbook of Physical Chemistry*, 2nd Ed., New York, D. Van Nostrand Co., 1946.

The major portion of the theoretical material for the work came from this source.

(3) Hallstrom, M. of, "Internal Pressure and the Heat of Vaporization of Liquids", *Ann. Acad. Sci. Fennice, Ser. A, II, No. 5*, 30 pp. (1942).

The author stated one theory of the effect of temperature on internal pressure.

(4) Hildebrand, J. H., "Solubility I - Internal Pressure and Solubility", *J. Am. Chem. Soc.*, *38*, 1452 (1916).

Deviations from Raoult's law are explained on the basis of differences in internal pressure.

(5) Hildebrand, J. H., "Solubility III - Relative Values of Internal Pressure and their Application", *J. Am. Chem. Soc.*, *41*, 1067-1080 (1919).

A method of calculating internal pressure from the heat of vaporization was included in this article.

(6) Hildebrand, J. H., "Solubility VI - Thermodynamic Relations Between Solubility and Internal Pressure", *J. Am. Chem. Soc.*, *43*, 500-507 (1921).

This reference provided a method of calculating relative internal pressure.

(7) Hildebrand, J. H., Benesi, A. H., and Mower, L. M., "Solubility of Iodine in Ethyl Alcohol, Ethyl Ether, Mesitylene, p-xylene, 2,2 dimethyl butane, Cyclohexane, and Perfluoroheptane", J. Am. Chem. Soc., 72, 1017-20 (1950).

An equation for predicting solubility from internal pressure data was given along with tables showing agreement between the theoretical and actual solubilities.

(8) Hildebrand, J. H., and Gjaldbaek, "The Solubility of Chlorine in Normal Perfluoroheptane and other Liquids", J. Am. Chem. Soc., 72, 609-11 (1950).

The relation between internal pressure, molal volume, and solubility was given in general terms.

(9) International Critical Tables, New York, McGraw Hill Book Co., Vol. IV, 1928, Vol. V, 1929, Vol. VII, 1930.

The data used in all calculations was obtained from this source.

(10) Leduc, A., "Internal Pressure in Gases", Compt. rend., 148, 1391-4 (1909).

In this article Leduc presented a constant temperature relationship for internal pressure.

(11) Leduc, A., "Internal Pressure in Gases", Compt. rend., 153, 179-82 (1911).

A corresponding temperature state relationship for internal pressure was included in this article.

(12) Leduc, A., "Internal Pressure in Gases", Compt. rend., 161, 97-100 (1915).

The effect of temperature on internal pressure was given in very general terms.

(13) Mc Clewis, W. C., "Internal Pressure - Latent Heat of Liquids", *Phil. Mag.*, *25*, 61-65 (1888).

Information on the range of the attractive forces between molecules was given.

(14) Mc Clewis, W. C., "Relation of Internal Pressure of a Liquid to its Dielectric Capacity and Permeability", *Phil. Mag.*, *28*, 104-16 (1889).

The effects of temperature on the orientation of molecules and on internal pressure were given in general terms.

(15) Mc Clewis, W. C., "Internal, Molecular, or Intrinsic Pressure - Survey of Various Expressions Proposed for its Determination", *Trans. Faraday Soc.*, *7*, 94-115 (1911).

The thermodynamic study of internal pressure was looked upon as being very far from complete.

(16) Stakhorskii, K., "The Molecular Pressure of Associated Molecules", *Urkrainskii, Khem. Zhurnal*, *1*, 544-52 (1925).

An empirical equation using only surface tension was presented.

(17) Stakhorskii, K. M., "Internal Pressure and Latent Heat of Vaporization of Liquids", *J. Russ. Phys. Chem. Soc.*, *58*, 966-82 (1926).

Van der Waals' constants at the critical temperature were used in an expression for internal pressure.

(18) Walden, P., "Relation Between Surface Tension, Heat of Evaporation, Internal Pressure, Boiling Point, and Diameter of Molecules", Ion, I, 402-12

A relationship was given relating internal pressure, surface energy, and molecular diameter.

(19) Walden, P., "Surface Tension, Internal Pressure and van der Waals' Constants a and b", Z. Physik. Chem., 66, 385-444 (1909).

Values of van der Waals' constants at the critical temperature were used in deriving an expression for internal pressure.

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