The use of the bimolecular equation, velocity = k[sugar][water] is shown to be unsound, and it is shown that the inversion velocity is best expressed by the equation, $dx/dt = k$ (sucrose molecules per molecule of water) (H^+ activity), for any particular inversion.

The decrease in water content and the increase in hydrogen-ion activity during inversion, are sufficient to explain the steady increase in the coefficients.

South Australia

[Contribution from the Chemical Laboratory of the University of California]

THE HEAT CAPACITY AND ENTROPY OF LEAD BROMIDE AND BROMINE

By Wendell M. Latimer and Howard D. Hoenshel

Received June 8, 1925 Published January 8, 1926

The purpose of this investigation was to obtain a more accurate experimental value for the entropy of bromine. At the time it was undertaken the only existing data were determinations of the average specific heat[1] of solid bromine from the boiling point of liquid hydrogen to that of liquid air, and from the latter point to 190°K. Since that time Eucken's coworkers[2] have investigated the specific heat of bromine; a discussion of their results will be included.

The entropy of bromine was determined by two independent methods.

1. The specific heat of solid bromine from 14°K. to its melting point was measured and the entropy calculated from the relation,

$$S = \int_0^T \frac{C_p}{T}\, dT = \int_0^T C_p\, d\, ln\, T$$

This expression was integrated by plotting C_p against $ln\ T$ and taking the area under the curve. Existing values for the entropy of fusion and the specific heat of liquid bromine were used to obtain the entropy at 298°K.

2. In a similar manner the entropy of lead bromide was determined, and the entropy of bromine calculated using this value, the entropy of lead and the ΔS for the reaction, $Pb + Br_2 = PbBr_2$, since we have, from the third law of thermodynamics, $S_{Pb} + S_{Br_2} = S_{PbBr_2} + \Delta S$. ΔS was determined from the experimental values for the change in free energy ΔF and the change in heat content, ΔH, of the reaction employing the relation, $T\Delta S = \Delta H - \Delta F$.

Since both the substances investigated retain a large portion of their

---

[1] (a) Dewar, *Proc. Roy. Soc.* (London), **76**, 325 (1905). (b) Barschall, *Z. Elektrochem.*, **17**, 341 (1911). (c) Koref, *Ann. Physik*, **36**, 49 (1911). (d) Estreicher and Staniewski, *Krakauer Anzeiger*, **1912**, p. 834.

[2] Suhrmann and Lüde, *Z. Physik*, **29**, 71 (1924).

heat content down to very low temperatures, it is desirable to carry the measurements to as low temperatures as possible. A temperature of 14°K., the triple point of hydrogen, was attained by boiling liquid hydrogen under reduced pressure. The liquefaction apparatus was that described by Latimer, Buffington and Hoenshel.[3] The liquefier was built in connection with the calorimetric apparatus in such manner that the cooling effect of the expanding gas above the liquefying point was utilized, and the trouble and loss arising in a transfer of the liquid hydrogen was avoided.

Experimental Part

Method.—The vacuum calorimeter method was used, with such adaptations as appeared advisable in this particular problem. The material was placed in a small metal calorimeter vessel, isolated from its surroundings by a high vacuum; a measured amount of electrical energy was supplied, and the rise in temperature noted.

In the case of lead bromide, a thin-walled copper calorimeter can, containing some 237 g. of the material, was used. This material was prepared by precipitation from c. p. lead nitrate and potassium bromide. It was thoroughly washed, and dried for several days at 120°. The resulting fine powder was tightly packed into the calorimeter. In order to provide rapid thermal conduction through the mass of the material, several radial vanes had been soldered into the can. As a further aid, it was filled with hydrogen just before it was soldered shut.

A silver can was employed for the bromine. Hard solder was used throughout, except for the final seal, which was above the level of the bromine. Otherwise, the construction was that described above. As a further precaution against corrosion, the bromine was frozen immediately, and was kept in that condition during the entire course of the experiments. After the measurements on solid bromine had been obtained, an attempt was made to investigate the liquid, but the vapor attacked the soft solder joint on the cover after one determination. The capacity of the calorimeter was approximately 216 g. C. p. bromine, distilled from phosphorus pentoxide, was used.

Temperature measurements were made in terms of a resistance thermometer. In making the choice between a resistance thermometer and thermocouple, it was believed that the former gives a better average value of the temperature of the calorimeter while it is more sensitive and much less affected by heat leaks through the connecting wires. The resistance thermometer was constructed of fine lead wire. This choice is due to the fact that the approximate linear relation between the resistance of lead and the temperature holds to a lower temperature than for any other metal. Wire of 0.017 mm. diameter was made by forcing the heated metal through a small hole under pressure. For simplicity, this same resistance was also used to supply heat to the calorimeter.

The wire was wound on the outside of the can, covering the entire length. For insulation a layer of very porous rice paper saturated with thick Bakelite lacquer was first baked onto the can. Over this the lead

---

[3] Latimer, Buffington and Hoenshel, This Journal, **47**, 1571 (1925).

wire was wound, the turns being separated from one another by an alternate winding of silk thread. It was then covered with another layer of Bakelite and paper, which served as protection against oxidation by the air, as well as afforded better heat conduction away from the wire. The whole was then covered with a layer of very thin copper foil, to lessen exchange of radiation with the surroundings. This sheath was soldered to the bottom of the can, to provide thermal contact. External connection with the thermometer was made through two d.s.c. B. and S. No. 30 copper wires, which were attached to the lead below the Bakelite covering.

The arrangement of the calorimetric apparatus is shown to scale in Fig. 1.

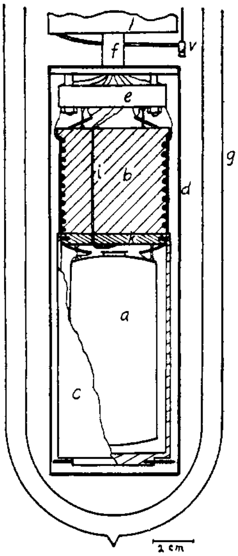

Fig. 1.

The can *a* was suspended by means of silk threads from the bottom of the large lead block *b*. To provide environment of an even temperature, the can was surrounded by the copper radiation shield *c*. During a run this shield was maintained at a practically constant temperature approximately equal to that of the calorimeter. This constancy was accomplished by thermally isolating it, and providing a large heat capacity, in the heavy block *b*. Four boxwood pegs, inserted in the bottom of the shield, prevented it from touching the outside can. Thermal contact was provided with the block by fastening the shield, by means of small screws,[4] to the tightly fitting copper plate *k*, which in turn was soldered to the lead block. Lead was used for this block because of the high value of its specific heat at low temperatures. This block was suspended by silk threads to the auxiliary block *e*, which in turn was fastened by copper studs to the cover of the outside can. The outside can *d* was fastened to the cover by means of a vacuum-tight soldered joint, and the entire apparatus evacuated through the tube *f*. The can and cover were of brass and the tube of steel. The steel tube was connected through a de Khotinsky seal to the glass line leading to the mercury diffusion pump. A pressure of less than 5×10^{-5} mm. was maintained during the determinations.

The end of the hydrogen liquefying interchanger *l* and the expansion valve *v* are shown just above the outside can. The whole apparatus is immersed in the Dewar tube *g* in a cold bath as nearly as possible at the temperature of the calorimeter. The following baths were used: 14–20°, liquid hydrogen under reduced pressure; 20–40°, liquid hydrogen; 40–70°, liquid air under reduced pressure; 70–130°, liquid air; 130–273°, ether cooled with liquid air; 273°, water. Above 157° (the melting point of ether) the temperature of the bath of liquid ether was so regulated as to be almost that of the block.

The wire leads were brought into the glass line through a de Khotinsky seal, and were carried to the apparatus through the tube *f*. To prevent an excessive amount

---

[4] It will be observed that where thermal contact between metal surfaces was desired, a soldered joint was employed when possible. When this could not be done, some other positive device, such as fastening by screws, was used. It was the experience of the authors that only thus could a constant and reliable thermal contact be obtained.

of heat leaking down the connecting wires, they were wrapped in individual grooves around the auxiliary lead block *e*, and covered with Bakelite lacquer to insure good thermal contact. This block was in sufficiently good contact with the top of the can to be maintained at the temperature of the bath.

The four connecting wires to the can were soldered to two wires at the top of the main block, making these junctions, in effect, the terminals of the resistance thermometer. This is permissible only when the resistance between these junctions and the thermometer proper is negligible in comparison with that of the thermometer. This was accomplished by using B. and S. No. 16 copper wire. This wire was cemented with Bakelite into sunken grooves in the lead block to prevent heat leak through from the auxiliary block. To minimize conduction from the block to the calorimeter, the final connection to the thermometer was made through two short pieces of B. and S. No. 40 copper wire.

The temperature of the block was measured by a thermocouple, which was brought through the small hole *i* and soldered to the bottom of the block. The grooved surface of the block was covered with lead foil, and on this was wound a constantan heater of about 100 ohms. This was cemented in place with Bakelite and covered with a thin copper sheath to lower radiation. The method of supplying and measuring the energy input and the method of measuring the resistance of the thermometer were those described by Gibson and Giauque.[5]

The following measurements give an idea of the efficiency of this calorimeter. At liquid-air temperatures the heat leak was about 0.02 cal. per minute per degree differential between the calorimeter and its surroundings. During a run, when this differential became as high as 2.5°, the heat leak was constant to 0.005 cal. for a period of 20 minutes. The calorimeter reached an equilibrium state after the heating current was shut off in from three to eight minutes. At liquid-hydrogen temperatures the heat leak was somewhat greater, due to the increased conductivity of gases at these low temperatures. As room temperature was approached the heat leak increased rapidly because of the increasing radiation losses. As a consequence this type of calorimeter cannot be employed with any satisfaction much above 0°C.

Calibration of Resistance Thermometers.—Before being used, the lead thermometers were heated for several days at 120° to minimize the slow increase in resistance always noted in lead. They were further tempered by being alternately dipped in liquid air and warmed to room temperature a dozen times. Although the resistance slowly increases with time, the value of the ratio R/R_0, where R_0 is the resistance at 0°C., remains constant. Hence resistances are always expressed in terms of this ratio, and R_0 was frequently determined for each thermometer.

The method of calibration generally employed by other investigators is to obtain the resistance of a lead thermometer at the boiling point of hydrogen, and at the melting point of ice. The values of R/R_0 for the range between are then calculated, by means of the Nernst α-rule,[6] from existing

[5] Gibson and Giauque, THIS JOURNAL, **45**, 93 (1923).

[6] Nernst, *Sitzber. preuss. Akad. Wiss.*, **1911**, 313.

data on the resistance of lead. This method, however, failed to represent the resistance of the lead used in this investigation with any degree of accuracy, thus necessitating a careful calibration over the entire range.

For the lower temperature range, the fixed points used in the calibration were the triple point and boiling point of hydrogen. The temperature at the triple point was taken as 13.94°K.,[7] and that at the normal boiling point as 20.39°K.[8]

Table I

The Relation between Temperature and Resistance for the Lead Thermometer

T, ° A.	R/R_0	$[d(R/R_0)]/dt$	T, ° A.	R/R_0	$[d(R/R_0)]/dt$
14	0.01102	0.00263	160	0.5604	0.00378
20	.02937	.00338	170	.5976	.00379
30	.06615	.00385	180	.6350	.00381
40	.1052	.00397	190	.6726	.00384
50	.1453	.00399	200	.7111	.00387
60	.1846	.00393	210	.7504	.00389
70	.2234	.00382	220	.7897	.00391
80	.2612	.00374	230	.8289	.00393
90	.2986	.00372	240	.8683	.00396
100	.3360	.00372	250	.9080	.00398
110	.3735	.00372	260	.9476	.00400
120	.4107	.00373	270	.9875	.00402
130	.4479	.00373	280	1.0278	.00404
140	.4852	.00373	290	1.0684	.00406
150	.5227	.00376	300	1.1091	.00408

The observed boiling points were corrected to 760 mm. pressure by means of the vapor-pressure measurements of Cath and Onnes. From 20°K. to room temperature the thermometers were compared with a copper-constantan thermocouple, calibrated in terms of the laboratory standard couple.[9] The temperatures between 80° and 20°K. were obtained by measuring the thermocouple at the triple point and boiling point of hydrogen and extending the thermocouple curve to these points. The temperatures in the middle of this range were necessarily somewhat uncertain. It was later found that all of the specific-heat curves had a break in this region, and the temperatures were so changed as to smooth out these breaks. This change in no case exceeded 0.2°, and the new values furnished just as likely an extrapolation of the thermocouple curve as did the values first chosen.

The results of the calibration of Thermometer 1, as typical, appear in Table I. The rate of change of R/R_0 with the temperature is given in Col. 3. When these values are plotted against the temperature a fairly sharp maximum occurs in the region between 20° and 80°K., where the

[7] Simon, *Z. Physik*, **15**, 307 (1923).

[8] Cath and Onnes, *Comm. Phys. Lab. Leiden*, No. 152a (1917).

[9] See Eastman and Rodebush, This Journal, **40**, 489 (1918).

thermometer could not be calibrated directly. A displacement of this maximum by as much as 0.2° causes a very noticeable break in the resulting heat-capacity curves. As mentioned above, this fact was made use of in the calibration of the thermometers.

Results.—The method of calculating the heat capacities, using Newton's law of cooling to correct for heat losses, was that described by Gibson and Giauque.[4] The results are given in Tables II and III.

TABLE II

BROMINE

Temp. °K.	C_p per mean g. atom	Temp. °K.	C_p per mean g. atom	Temp. °K.	C_p per mean g. atom
14.9	0.914	88.8	4.91	144.8	5.79
17.3	1.18	90.5	5.05	148.8	5.85
20.2	1.52	92.0	5.08	152.7	5.90
23.3	1.91	93.5	5.15	175.4	6.13
26.6	2.25	94.4	5.14	179.2	6.20
29.9	2.59	96.0	5.16	183.0	6.27
33.1	2.90	97.1	5.23	209.3	6.56
48.6	3.98	98.5	5.19	214.2	6.61
51.9	4.16	100.9	5.27	217.8	6.62
55.3	4.33	108.6	5.37	244.2	7.01
65.5	4.69	108.6	5.37	245.2	6.96
68.4	4.73	112.5	5.42	247.4	7.02
71.8	4.73	112.6	5.44	248.6	7.09
75.4	4.83	116.5	5.47	250.6	7.12
88.1	5.03	116.6	5.47	252.4	7.18

TABLE III

LEAD BROMIDE

Temp. °K.	C_p per mean g. atom	Temp. °K.	C_p per mean g. atom	Temp. °K.	C_p per mean g. atom
18.4	1.22	80.6	5.05	215.2	6.14
23.9	1.72	96.7	5.43	218.9	6.19
28.5	2.12	99.0	5.43	245.6	6.25
32.1	2.41	103.1	5.51	249.4	6.28
39.6	3.15	107.2	5.53	253.1	6.23
43.2	3.47	122.4	5.67	274.8	6.33
46.8	3.75	126.4	5.66	278.7	6.35
50.4	4.01	130.2	5.70	281.9	6.35
51.2	4.05	149.4	5.83	284.3	6.48
55.5	4.33	153.3	5.87	287.0	6.47
59.4	4.49	157.3	5.89	289.3	6.13
63.1	4.64	182.0	6.00	289.9	6.40
66.8	4.74	186.6	6.04	293.1	6.34
70.5	4.87	190.3	6.07	295.6	6.48
73.6	4.94	211.7	6.18	297.0	6.34
77.0	4.85				

Figs. 2 and 3 show the curves obtained by plotting the heat capacities of bromine and lead bromide against the logarithm of the temperature.

The average deviation of the points from the best curve is a few tenths of a per cent., if we except three points which are obviously in error.

All experimental evidence indicates that at sufficiently low temperatures the relation between the specific heat and the temperature for all substances is expressed as $C_p = aT^b$, where a and b are constants characteristic of the substance. For metals the expression becomes the Debye T^3 rule. When log C_p is plotted against log T this relation gives a straight line of slope b. For both lead bromide and bromine such a plot was made for the last few values of the heat capacity. In each case the points are very accurately represented by a straight line. The values of b given by the slopes of these lines are used to extrapolate the heat capacities to the absolute zero. The value of b for bromine was 1.66 and for lead bromide, 1.21.

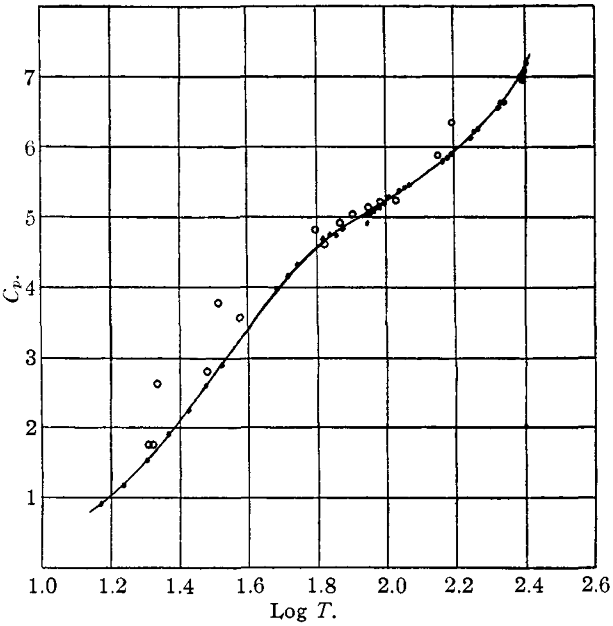

Fig. 2.—Bromine, ○ = Suhrmann and Lüde.

For bromine the area under the curve in Fig. 2 from $T = 14.12°$ to $T = 265.9°$, when multiplied by 2.303 to convert to natural logarithms, is 12.15. The extrapolation from 15.85° to 0° by means of the value of $b = 1.66$ for the equation $C_p = aT^b$ gives for the entropy 0.510. This value was cut to 0.45 to allow for an approach to the T^3 rule at lower temperatures. The resulting value of S at the melting point is 12.60. Regnault's[10] values[9] of 1290 cal. for the heat of fusion, and 8.4 for the heat capacity of liquid bromine between the melting point and 298°, were em-

[10] Regnault, *Ann. chim. phys.*, **8**, 27 (1849).

ployed. The first value was closely checked by calculations made by Lewis and Randall[11] from vapor-pressure data. From these data we have $S_{298} = 12.60 + 4.85 + 0.95 = 18.4 \pm 0.2$ cal. per degree.

The experimental values obtained by Suhrmann and Lüde[2] for the heat capacity of bromine are shown by the circles in Fig. 2. The entropy of bromine was calculated by the authors in a manner similar to that employed above, from the curve drawn by Suhrmann and Lüde from their data, augmented at the higher temperatures by the old data for the average heat capacity. The value thus obtained was 18.6, an agreement which seems rather fortuitous after an inspection of the data.

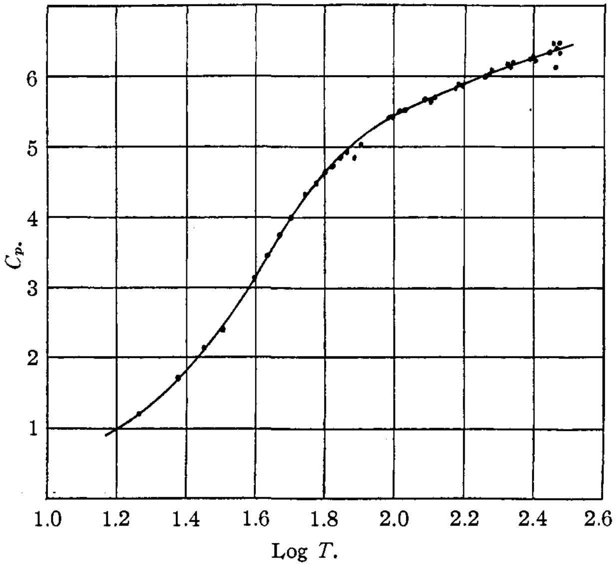

Fig. 3.—Lead bromide.

The entropy of lead bromide from 15.85° to 298°K., from the curve in Fig. 3, is 12.43. The value from 15.85° to 0°, extrapolated from the graphically determined value of the exponent b, is 0.861. For reasons similar to those stated in the case of bromine, this value was cut to 0.80. Therefore $S_{298} = 12.43 + 0.80 = 13.23 \pm 0.15$ entropy units per mean gram atom, or 39.7 ± 0.45 entropy units per mole. This is in close agreement with the value, 39.2, calculated by Latimer[12] from the entropy of lead and bromide ions.

To obtain the entropy of bromine, we require S_{298} for lead, and ΔH and ΔF for the reaction,

$$Pb + Br_2 = PbBr_2 \qquad (1)$$

---

[11] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923,** p. 515.

[12] Latimer, This Journal, **43,** 818 (1921).

The value of S_{298} for lead[13] is taken as 15.53. For the reaction,

$$Pb + 2HgCl + 2Br(0.1M) = PbBr_2 + 2Hg + 2Cl^{-}(0.1M) \qquad (2)$$

Lewis and Brighton[14] found $E = 0.551$. Making an estimated correction of 0.002 for the appreciable solubility of lead chloride in potassium chloride on the calomel side, $E = 0.549$. Hence, $\Delta F_{298} = 25{,}330$. For the ΔF_{298} of formation from the elements of mercuric chloride and the ions of bromine and chlorine we find, respectively, —25,137, —24,595 and 31,367,[15] from which ΔF_{298} of lead bromide = —62,065.[16]

The following three determinations have been made for ΔH_{298} of lead bromide: (1) —64,456 (Thomsen),[17] (2) —66,350 (Braune and Koref),[18] (3) —65,580 (Krahmer, Webb). The first two are direct calorimetric determinations. The third is derived from an electrometric determination by Krahmer[19] of ΔH_{298} for the reaction, $Pb + 2AgBr = 2Ag + PbBr_2$. $\Delta H = —17{,}960$ cal., and a calorimetric determination of the heat of formation of silver bromide by Webb.[20] This value is 23,810 cal.

The values of S_{298} for bromine, calculated from these various heats of reaction, are given below.

ΔH_{298} of lead bromide,	−64,456 (Thomsen),	−66,350 (Braune and Koref),	−65,580 (Krahmer, Webb)
S_{298} of bromine	16.09	19.27	17.98

If we discard Thomsen's value as being the least trustworthy, we obtain as an average value $S_{298} = 18.6 \pm 1.0$. This is in good agreement with the value obtained by the direct method, $S_{298} = 18.4 \pm 0.2$.

Summary

An apparatus for measuring specific heats at low temperatures is described.

The temperature-resistance relations for two lead resistance thermometers are given.

The heat capacities of bromine and lead bromide have been determined from 14°K. to room temperature. These values give for the entropy of bromine $S_{298} = 18.4 \pm 0.2$ cal. per degree, and for lead bromide $S_{298} = 13.25 \pm 0.15$ cal. per degree per average gram atom.

Using this value for the entropy of lead bromide, and thermal data for

---

[13] Lewis, Gibson and Latimer, THIS JOURNAL, **44**, 1008 (1922).

[14] Lewis and Brighton, *ibid.*, **39**, 1906 (1917).

[15] Ref. 11, p. 607.

[16] Gerke [*Chem. Reviews*, **1**, 395 (1925)] has recently published data on a cell in which Reaction 1 should take place. These data lead to a value of 62,000 for ΔF_{298} of lead bromide. Although the temperature coefficient of E for this cell leads to an unquestionably high value for the heat of the reaction, it is probable that E itself is quite accurate.

[17] Thomsen, *J. prakt. Chem.*, [2] **12,** 92 (1875).

[18] Braune and Koref, *Z. anorg. Chem.*, **87,** 175 (1914).

[19] Krahmer, *Z. Elektrochem.*, **26,** 97 (1920).

[20] Webb, *J. Phys. Chem.*, **29,** 816 (1925).

the formation of lead bromide from its elements, an independent value for the entropy of bromine is found, $S_{298} = 18.6 \pm 1.0$ cal. per degree.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 175]

A MASS ACTION EQUATION FOR COMPRESSED GASES, WITH APPLICATION TO THE HABER EQUILIBRIUM DATA

BY LOUIS J. GILLESPIE

RECEIVED JUNE 13, 1925 PUBLISHED JANUARY 8, 1926

Recently the following equation was derived[1] for the fugacity (f_e) of a gas in a mixture, from the assumptions that at sufficiently low pressures the equilibrium pressure of a gas in a mixture (or its "partial pressure") approaches the mole fraction—total pressure product and the fugacity approaches the pressure.

$$RT\, ln\, f_e = \int_{p^\times}^{p} (\partial v/\partial n_1 - v_1/n_1)\mathrm{d}p + RT\, ln\, f_p + RT\, ln\, x_1 \qquad (1)$$

Here f_p is the fugacity of the pure gas at the total pressure of the mixture, x_1 is the mole fraction, $\partial v/\partial n_1$ is the partial molal volume of the gas in the mixture, and v_1/n_1 is the molal volume of pure gas, the molal and partial molal volumes being measured at the same pressure (p). The integration is at constant temperature and composition and is carried from a very low pressure $p^\times$ up to the total pressure of the mixture. Utilizing the definition of fugacity and adding and subtracting the term $\int_{p^\times}^{p} (RT/p)\mathrm{d}p$, we obtain

$$RT\, ln\, f_p = \int_{p^\times}^{p} (v_1/n_1)\mathrm{d}p + RT\, ln\, p^\times = \int_{p^\times}^{p} (v_1/n_1 - RT/p)\mathrm{d}p + RT\, ln\, p \qquad (2)$$

Substituting in Equation 1 and simplifying, we have

$$ln\, f_e = (1/RT)\int_{0}^{p} (\partial v/\partial n_1 - RT/p)\mathrm{d}p + ln\, px_1 \qquad (3)$$

To find the mass action expression, let ν_1 denote the stoichiometrical coefficient of Substance 1 in a chemical equation, these coefficients being taken negative for disappearing species, and let K_p and K_f be the usual mass action expressions in terms of "partial pressures" (px_1) and fugacities, respectively. Summation for all the species gives us

$$\Sigma\nu_1\, ln\, f_e = ln\, K_f = ln\, K_p + (1/RT)\Sigma\nu_1 \int_{0}^{p} (\partial v/\partial n_1 - RT/p)\mathrm{d}p \qquad (4)$$

Equation 4 is a general mass action expression for pressure and concentration effects at constant temperature, since K_f must be a function of the temperature alone. The integration is subject to the same conditions as before, the constant compositions being equilibrium compositions.

---

[1] Gillespie, THIS JOURNAL, **47,** 305 (1925).