Application of Thermodynamics to Chemical Problems Involving the Oxide Cathode

Addison H. White

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thermionic vacuum tube is suitable for the immediate purposes. The pertinent geometric data obtained from the dismantled tube are:

Grid strand radius, $R_G=0.00825$ cm,
Grid strand pitch, $n_G=2.53$ strands/cm,
Grid to plate distance, $b=0.239$ cm,
Filament to grid distance, $a=0.195$ cm,
Filament strand radius, $R_C=0.0128$ cm,
Filament strand pitch, $n_C=2$/cm.

The filament wire pitch is derived from an equivalent model. The actual filament configuration in the chosen thermionic vacuum tube is an inverted W shape filament, 13.0 cm long. To simplify the analysis it was considered valid, in the light of the assumption that $S_C \ll S_G$, to treat the actual filament geometry as symmetrically disposed parallel strands orthogonal to the grid wires as shown in Fig. 4.

The plate characteristics of the chosen thermionic vacuum tube are illustrated by Fig. 5.

The potential function (8) is evaluated for this tube in the following manner: The values of the potential coefficients (12a) through (12d) in expressions (11) are computed by merely substituting the corresponding geometric constants and potential differences. Then, the charges τ_C' and τ_P'' in expressions (11) are solved for and substituted in the potential function, (8). From the foregoing geometric data it is evident that

$$S_C'=\cosh 2\pi n_C R_C=1.013,$$
$$S_G''=\cosh 2\pi n_G R_G=1.008,$$
$$R_C'=\sinh 2\pi n_C R_C=0.1607, \text{ and}$$
$$R_G''=\sinh 2\pi n_G R_G=0.1304.$$

The selected operating point with reference to Fig. 5 is defined by

$$E_P=100 \text{ volts},$$
$$E_G=-10 \text{ volts, and}$$
$$E_C=0.$$

These are substituted in expressions (11) to yield the charges,

$$(-\tau_C')=-.0138 \text{ statcoulomb}$$

and

$$(+\tau_P'')=+.0678 \text{ statcoulomb.}$$

Upon substitution of these charges in expression (8) with pertinent other factors the potential function,

$$E=-0.0138\left\{\ln\frac{0.0258}{\left|1.013\pm\frac{1}{r'}\right|\left|r'\pm 1.013\right|}+0.790\ln\left|1.008r''\pm 1\right|\right\}+0.0678\ln\left|\frac{r''}{1.006}\pm 1\right|,$$

is obtained.

This particular potential function is next evaluated, with the previously fixed values of E_P, E_G and E_C, for the following four important cases, between plates along a path (a) halfway between grid and filament strands, i.e. for $\phi'=\phi''=\pi$, (b) halfway between grid strands though centrally through the filament strands, i.e. for $\phi'=0$, $\phi''=\pi$, (c) halfway between the filament strands though centrally through the grid strands, i.e. for $\phi'=\pi$, $\phi''=0$, and (d) centrally through the grid and filament strands, i.e. for $\phi'=\phi''=0$.

It should be recalled that the choice of sign in the absolute terms are dependent upon the chosen values of ϕ' and ϕ''. As previously mentioned, only the two extreme values of these angles were selected. So that whenever these angles are equal to π, in the Z plane, the signs in the absolute terms are simply positive, whereas when zero the sign chosen is negative.

The final results are illustrated by Fig. 6 through 9 and are self-explanatory.

Application of Thermodynamics to Chemical Problems Involving the Oxide Cathode

Addison H. White
Bell Telephone Laboratories, Murray Hill, New Jersey

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Computations of the free energy of some chemical reactions involving dissociation or reduction of alkaline earth oxides have been made on the basis of rough estimates of the thermochemical quantities which have not been measured. The resulting values of free energy, equilibrium constant and equilibrium pressure of barium vapor derived for specified ideal conditions are tabulated. Several applications of these results are discussed.

I. INTRODUCTION

THE oxide-coated cathode is a complex system whose chemistry and physics are still the subject of extensive investigation.[1] Over the long history of research in this field there has been very little application of the powerful methods of thermodynamics to the chemistry of reactions involving these alkaline earth oxides.[2] The primary reason for this is the lack of thermochemical data, particularly the high-temperature heat capacities of BaO and SrO. Nevertheless, it is

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[1] J. P. Blewett, J. App. Phys. **17**, 643 (1946).

[2] For a review of such applications, see J. P. Blewett, J. App. Phys. **10**, 831 (1939); see also reference (12).

possible to base illuminating calculations on reasonable estimates of such quantities. This paper is designed to provide a tabulation of the results of such calculations made several years ago which, it has since developed, are of interest to a number of workers in the field. It must be emphasized that the free energies of reaction thus derived are only approximations, but at a rough guess are correct to within five kilocalories per mole of BaO or SrO involved.

II. METHOD OF COMPUTATION

The change of the Gibbs free energy accompanying a chemical reaction is

$$\Delta F^{\circ}(T)=\Delta H(T)-T\Delta S(T), \qquad (1)$$

where H and S are respectively the heat content and the entropy.[3] The superscript o indicates as usual that each substance involved in the reaction is conceived to be in its standard state. It is thus sufficient for the calculations below to know ΔH and ΔS for the reactions and temperatures in question. One convenient way to obtain these quantities is to start with the known values of $\Delta H(T_0)$ and $\Delta S(T_0)$ ($T_0=298.1°\mathrm{K}$) in calculating the desired quantities at the higher temperatures of interest, according to

$$\Delta H(T)=\Delta H(T_0)+\int_{T_0}^{T}\Delta C_p dT; \qquad (2)$$

$$\Delta S(T)=\Delta S(T_0)+\int_{T_0}^{T}\Delta C_p d\ln T. \qquad (3)$$

ΔC_p is the total molar heat capacity at constant pressure of the substances "produced" less that of those "consumed" in the reaction. The molar heat capacities C_p of the substances involved below can all be expressed in the approximate analytical form*

$$C_p=A+BT-CT^{-2}+DT^{-\frac{1}{2}}$$

so that, for any of the reactions involved,

$$\Delta C_p=\Delta A+\Delta BT-\Delta CT^{-2}+\Delta DT^{-\frac{1}{2}}. \qquad (4)$$

Equations 1 to 4 yield, after the indicated integrations

$$\Delta F^{\circ}(T)=\Delta H(T_0)-T\Delta S(T_0)$$
$$+f_A\Delta A+f_B\Delta B+f_C\Delta C+f_D\Delta D \qquad (5)$$

where

$$f_A=T-T_0-T\ln(T/T_0),$$
$$f_B=TT_0-\tfrac{1}{2}(T^2+T_0^2),$$
$$f_C=1/2T-(1/T_0)(1-T/2T_0),$$
$$f_D=4T^{\frac{1}{2}}-2TT_0^{-\frac{1}{2}}-2T_0^{\frac{1}{2}}.$$

These functions of temperature are presented in Fig. 1 with sufficient accuracy for calculations of this type.

The thermochemical data used here are recorded in Table I, together with the sources from which they were obtained. It will be noted below that some of the heat capacity data are employed beyond the temperature range of their validity as specified by the last column of the table. Where data are lacking, the basis of an estimate is briefly indicated in the footnotes appended to the table. In particular the high-temperature molar heat capacities of BaO and SrO are taken to be equal to that of CaO, which has been measured. This is empirically justified by the fact that at 298.1°K the three heat capacities fall within the range from 10.23 to 11.34 calories per degree-mole, and that below room temperature this range decreases with increasing temperature.[4]

The values of free energy obtained as above for twelve chemical reactions at four elevated temperatures are recorded in Table II. The free energy of formation of water in Row 1 is useful for obtaining the free energy for reactions not included here by addition or subtraction according to the standard procedure.[3] Reaction 2 does not occur but is similarly useful in combination with other reactions. Reactions 3 to 12 are relevant to various aspects of the oxide cathode problem.

III. THERMAL DISSOCIATION OF ALKALINE EARTH OXIDES

In order to illustrate the application of the data to problems of interest the equilibrium constants of these reactions have been calculated according to

$$\Delta F^{\circ}=-RT\ln K,$$

and are recorded in Table III. One problem is to esti-

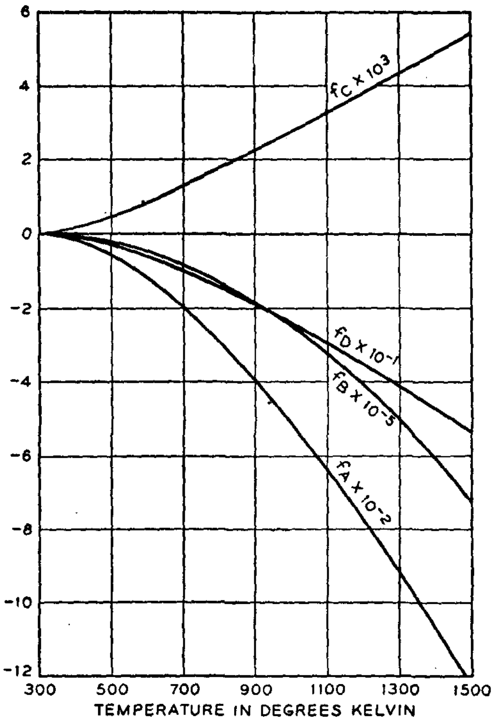

FIG. 1.

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[3] See e.g., G. N. Lewis and M. Randall, *Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1923).

* See Table I, reference (d).

[4] Table I, reference (c).

TABLE I. Thermochemical data employed in free energy calculations.

	$H(T_0)$[a] (Kilocalories/Mole)	$S(T_0)$[c] (E.U./Mole)	$C_p=A+BT-CT^{-2}+DT^{-\frac{1}{2}}$ (calories deg.$^{-1}$ mole^{-1}). A[d]	$B\times10^3$[d]	$C\times10^{-5}$[d]	D[e]	Valid range
H_2	0	31.23	5.797[e]	1.003[e]	0	+14.63	273°–2500°K
O_2	0	49.03	9.629[e]	0.369[e]	0	−42.83	300°–2500°
$H_2O(g)$	−57.798[f]	45.17	8.828[e]	1.917[e]	0	−29.58	300°–2500°
$CH_4(g)$	−19.100	44.46	5.34	11.5	0	0	273°–1200°
$CO(g)$	−26.428	47.32	7.74[e]	0.74[e]	0	−20	273°–2500°
$Ba(g)$	(+44.500)[g]	40.67	4.97	0	0	0	All
$BaO(s)$	−133.100	16.8	10.0[h]	4.84[h]	1.080[h]	0	
$Ni(s)$	0	7.1	6.99	0.905	0	0	626°–1725°
$NiO(s)$	−57.830	9.25[i]	13.69[j]	0.83[j]	2.915[j]	0	273°–1373°
$C(gr)$	0	1.36	2.673	2.617	1.169	0	273°–1373°
$Si(s)$	0	4.50	5.74	0.617	1.01	0	273°–1174°
$SiO_2(l)$	−198.300	11.2	12.80	4.47	3.02	0	273°–1973°
$BaSiO_3(s)$	−356.040	28[k]	27.95[l]	2.056[l]	7.456[l]	0	
$Mg(g)$	+35.907[b]	35.51	4.97	0	0	0	All
$MgO(s)$	−145.760	6.4	10.86	1.197	2.087	0	273°–2073°
$Sr(g)$	(+39.2)[m]	39.33	4.97	0	0	0	All
$SrO(s)$	−140.700	13.0	10.0[h]	4.84[h]	1.080[h]	0	
$Ca(g)$	+42.485[b]	37.00	4.97	0	0	0	All
$CaO(s)$	−151.710	9.5	10.00	4.84	1.080	0	273°–1173°

[a] International Critical Tables, Vol. V, p. 169 (1929), unless otherwise specified.
[b] K. K. Kelley, U. S. Bureau of Mines Bulletin 383 (1935).
[c] K. K. Kelley, U. S. Bureau of Mines Bulletin 394 (1936), unless otherwise specified.
[d] K. K. Kelley, U. S. Bureau of Mines Bulletin 371 (1934), unless otherwise specified.
[e] M. deK. Thompson, *Total and Free Energies of Formation of the Oxides of Thirty-two Metals* (Electrochemical Society, New York, 1942).
[f] F. D. Rossini, J. Research, Nat. Bur. Stand. 22, 407 (1939).
[g] Heat of sublimation assumed independent of temperature and equal to Van Liempt's value, 800°–1050°K (J. A. M. Van Liempt, Rec. Trav. Chim. de Pay-Bas. 55, 468 (1936).
[h] Assumed equal to values for CaO, $300° < T < 1500°$.
[i] Seltz, DeWitt, and MacDonald, J. Am. Chem. Soc. 62, 3527 (1940).
[j] A. F. Kapustinski and K. A. Novosel'tsev, J. Phys. Chem. USSR 11, 61 (1938).
[k] Assumed equal to the sum of $S(T_0)$ for BaO and SiO_2, by analogy with the result observed in $CaSiO_3$.
[l] Assumed equal to values for Wollastonite, $CaSiO_3$, $273° < T < 1573°$.
[m] Taking heat of vaporization of liquid strontium from (*b*) to be 37.046 kilocalories at 298°K, and adding the observed heat of fusion of strontium at 1030°K of 2.190 kilocalories, assuming it to be equal to heat of fusion at 298°K.

mate the pressure of gaseous Ba and O_2 in equilibrium with solid BaO at 1273°K, as compared with its molecular vapor pressure of 4×10^{-7} mm.[5] For this we have to a good approximation[3]

$$K=p_{Ba}{}^2p_{O_2} \tag{6}$$

where the equilibrium partial pressures identified by the subscripts are expressed in atmospheres. For the ideal case with no source of Ba or O_2 except the dissociating BaO

$$p_{Ba}=2p_{O_2}=(2K)^{\frac{1}{3}}.$$

This pressure as listed under p_m in the table is 2×10^{-11} mm of mercury, showing that at 1273°K the rate of loss of BaO by dissociation to gaseous products is negligible compared with the loss by evaporation of BaO molecules. In SrO and CaO however similar estimates yield "dissociation pressures" p_m in Table III which are smaller than the vapor pressures by a factor of less than ten. In practice this is of little significance when the pressure of oxygen due to contamination is higher than that due to dissociation of the alkaline earth oxide, in experiments such as the determination of the vapor pressure of this oxide.

The equilibrium pressure of 8×10^{-17} mm of Ba or 4×10^{-17} mm of O_2 obtained by extrapolating the data of Table III to 1000°K may seem in conflict with Dushman's[6] estimate of $<10^{-40}$ atmosphere for the dissociation pressure of BaO at this temperature. However Dushman's result presumably refers to the conventional meaning of the term "dissociation pressure;" i.e., the equilibrium pressure of oxygen above the oxide in the presence of the *solid* metal. This may be obtained from Eq. (6) by setting p_{Ba} equal to the vapor pressure of solid Ba, 1.2×10^{-2} mm at 1000°K.[7] The equilibrium pressure of oxygen thus derived is 2×10^{-45} mm or 3×10^{-48} atmosphere, in agreement with Dushman. Since no such pressures are attainable it is of course concluded that no solid barium nor for that matter any significant concentration of excess barium dissolved in BaO can be obtained by thermal dissociation of BaO at or near 1000°K.

IV. PRODUCTION OF FREE BARIUM

A widely accepted theory of the oxide cathode starts with the assumption that BaO is an excess electronic semiconductor by virtue of a slight stoichiometric excess of barium atoms dissolved in it.[8] The possibility of supplying such excess barium by the reaction of various reducing agents with BaO has been considered from this thermodynamic point of view. The results are shown, in

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[5] A. Claassen and C. F. Veenemans, Zeits. f. Physik 80, 343 (1933).

[6] S. Dushman, Rev. Mod. Phys. 2, 433 (1930); vd. also J. A. Becker, Trans. Am. Electrochem. Soc. 59, 209 (1931) and Wagner, Electronics 1, 178 (1930).

[7] Table I, reference g.

[8] See e.g., J. P. Blewett, J. App. Phys. 10, 668 (1939) for a review; see also reference (10).

terms of the equilibrium pressure of barium vapor, by the data for Reactions 4 to 10 in Table III. The concentration of excess barium in the solid in equilibrium with this vapor can be estimated as to order of magnitude by assuming that Raoult's law holds over the entire range of solid solubility. Then, since the saturated solution would be in equilibrium with solid or liquid barium,

$$f_{\mathrm{Ba}}/f_{\mathrm{Ba}}{}^{\circ}=p_{\mathrm{Ba}}/p_{\mathrm{Ba}}{}^{\circ} \tag{7}$$

where f_{Ba} and $f_{\mathrm{Ba}}{}^{\circ}$ are, respectively, the equilibrium and the saturated mole fractions of dissolved barium, while $p_{\mathrm{Ba}}{}^{\circ}$ is the vapor pressure of solid or liquid barium. The value of $f_{\mathrm{Ba}}{}^{\circ}$ may be taken from Schriel to be of the order of 0.01 at 1400°K.[9] No estimates of f_{Ba} are included in Table III, since p_{Ba} is equally useful for comparing the effectiveness of the various reducing agents. By way of example however, the p_{Ba} of 1 mm at 1473°K obtained from Reaction 5, together with $p_{\mathrm{Ba}}{}^{\circ}=17$ mm and $f_{\mathrm{Ba}}{}^{\circ}=0.01$, yields 6×10^{-4} for the concentration of dissolved barium in equilibrium with 10^{-5} atmospheres of methane.

Reactions 4 and 5 represent procedures that might be employed in a laboratory experiment designed to increase the excess barium content of BaO. The equilibrium pressures of barium vapor tabulated in the last column show that methane at a pressure of 10^{-5} atmosphere is at least 100-fold more effective than hydrogen at one atmosphere in reducing BaO. The low pressure chosen for the methane calculation was that employed in an experiment which is described elsewhere.[10]

Reactions 6 to 10 are related to mechanisms by which BaO might be reduced in a commercial oxide cathode, where the (BaSr)O is in contact with a nickel core containing small concentrations of such impurities or additives as carbon, silicon, and magnesium. Reaction 6 shows that nickel itself can have no effect, since the equilibrium pressure of barium vapor above BaO alone is higher than that above BaO in the presence of both nickel and NiO. In Reaction 7 carbon is shown to have a considerable effect, although it should be emphasized that Reactions 7 to 10 are written for saturated solid solutions of the reducing agent in nickel, whereas the commercial concentrations are probably much lower. Reactions 8 and 9 show that silicon would be much less effective than carbon if it were not for the side reaction between BaO and SiO_2 to form a silicate, here assumed for convenience in calculation to be $BaSiO_3$ rather than the experimentally observed Ba_2SiO_4.[11] It will be noted that the equilibrium constants for Reaction 10 have been calculated for gaseous rather than liquid magnesium. However the barium pressures listed under p_m are derived by taking the pressure of magnesium to be that in equilibrium with its liquid at each temperature. The results are thus to be compared with those of Reactions 6 to 9 and show magnesium to be thermodynamically the most effective of the reducing agents considered here.

Tungsten is also of considerable interest as a reducing agent for alkaline earth oxides, but is not treated here in view of the careful work of Moore, Allison, and Morrison.[12]

TABLE II. Free energy changes accompanying certain reactions.

Reaction	ΔF° (Kilocalories) $T=873°$	1073°	1273°	1473°
1. $2H_2+O_2=2H_2O(g)$	−95	−90	−84	−79
2. $2CH_4+O_2=2CO+4H_2$	−91	−110	−128	−147
3. $2BaO(s)=2Ba(g)+O_2$	273	255	238	221
4. $2SrO(s)=2Sr(g)+O_2$	273	254	236	218
5. $2CaO(s)=2Ca(g)+O_2$	300	280	262	243
6. $BaO(s)+H_2=Ba(g)+H_2O$	89	82	77	71
7. $BaO(s)+CH_4=Ba(g)+CO+2H_2$	91	73	55	37
8. $BaO+Ni(s)=Ba(g)+NiO(s)$	98	93	88	84
9. $BaO(s)+C(gr)=Ba(g)+CO$	91	78	65	53
10. $2BaO(s)+Si(s)=2Ba(g)+SiO_2(l)$	111	102	93	84
11. $3BaO(s)+Si(s)=2Ba(g)+BaSiO_3(s)$	87	77	69	60
12. $BaO+Mg(g)=Ba(g)+MgO(s)$	1	2	4	6

V. CONCLUSION

This is not intended to be an inclusive discussion of the application of thermodynamics to the chemistry of

TABLE III. Equilibrium constants of various chemical reactions.

1 Reaction	2 T	3 K	4 p_m(mm)
1. $2BaO(s)=2Ba(g)+O_2$	1073	1×10^{-52}	6×10^{-15}
	1273	2×10^{-41}	2×10^{-11}
	1473	2×10^{-33}	1×10^{-8}
2. $2SrO(s)=2Sr(g)+O_2$	1073	2×10^{-52}	5×10^{-15}
	1273	3×10^{-41}	3×10^{-11}
	1473	4×10^{-33}	2×10^{-8}
3. $2CaO(s)=2Ca(g)+O_2$	1073	8×10^{-58}	9×10^{-17}
	1273	1×10^{-45}	1×10^{-12}
	1473	8×10^{-37}	9×10^{-10}
4. $BaO(s)+H_2(g)=Ba(g)+H_2O(g)$	1073	2×10^{-17}	3×10^{-6}
	1273	7×10^{-14}	2×10^{-4}
	1473	3×10^{-11}	4×10^{-3}
5. $BaO(s)+CH_4(g)=Ba(g)+CO(g)+2H_2(g)$	1073	2×10^{-15}	6×10^{-3a}
	1273	4×10^{-10}	1×10^{-1a}
	1473	4×10^{-6}	1^{a}
6. $BaO(s)+Ni(s)=Ba(g)+NiO(s)$	1073	1×10^{-19}	9×10^{-17}
	1273	7×10^{-16}	5×10^{-13}
	1473	4×10^{-13}	3×10^{-10}
7. $BaO(s)+C(\mathrm{graph})=Ba(g)+CO(g)$	1073	1×10^{-16}	8×10^{-6}
	1273	6×10^{-12}	2×10^{-3}
	1473	1×10^{-8}	9×10^{-2}
8. $2BaO(s)+Si(s)=2Ba(g)+SiO_2(l)$	1073	2×10^{-21}	3×10^{-8}
	1273	1×10^{-16}	8×10^{-6}
	1473	3×10^{-13}	4×10^{-4}
9. $3BaO(s)+Si(s)=2Ba(g)+BaSiO_3(s)$	1073	2×10^{-16}	1×10^{-5}
	1273	2×10^{-12}	1×10^{-3}
	1473	1×10^{-9}	3×10^{-2}
10. $BaO(s)+Mg(g)=Ba(g)+MgO$	1073	3×10^{-1}	7^{b}
	1273	2×10^{-1}	4×10^{b}
	1473	1×10^{-1}	2×10^{2b}

[a] In equilibrium with CH_4 at 10^{-5} atmosphere.

[b] In equilibrium with magnesium gas at the vapor pressure of liquid magnesium.

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[9] M. Schriel, Zeits. f. Anorg. allgem. Chemie **231**, 313 (1937).

[10] Hannay, MacNair, and White, J. App. Phys. **20**, 669 (1949); see also C. H. Prescott and J. Morrison, J. Am. Chem. Soc. **60**, 3047 (1938).

[11] A. Fineman and A. Eisenstein, J. App. Phys. **17**, 663 (1946); H. P. Rooksby, Nature **159**, 609 (1947).

[12] Moore, Allison, and Morrison, Phys. Rev. **75**, abstract in print; paper to be published; *cf.* also G. E. Moore, J. Chem. Phys. **9**, 427 (1941).

the oxide cathode, but rather to illustrate the type of problems that can be attacked profitably even without complete thermochemical data. However the data of Table II may be combined to obtain the free energies of a number of reactions not explicitly considered above. For example, Reaction 1 or Reaction 2 may be added to Reaction 4 to obtain the free energy for reduction of SrO by hydrogen or methane respectively; or Reactions 3, 5, and 9 may be combined to yield the free energy of reduction of CaO by graphitic carbon.

Finally, it is to be emphasized that equilibrium conditions are seldom attained; hence the barium pressures listed represent upper limits not likely to be experimentally realized.

The author is indebted to L. A. Wooten, C. Herring, and G. E. Moore for illuminating discussions of this subject.

Time Constants for Vacuum Gage Systems

S. A. Schaaf and R. R. Cyr
University of California, Berkeley, California

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A typical system for measuring pressures in a rarefied gas consists of a vacuum gage connected to the gas by a length of tubing, usually with an orifice of diameter smaller than that of the tubing at the end. The interior surface of this system will outgas at a fairly constant rate for a long period of time so that an equilibrium state will be reached with a definite non-constant pressure distribution along the tubing. The response time constant for the system to come to equilibrium and the difference in pressure between gas and gage are functions of the outgassing rate and the geometry of the system. An analysis is made assuming molecular flow, and formulas are obtained for the response time and the pressure difference. It is shown that there is an optimum value of the tubing diameter for a given orifice diameter, gage volume, and length of tubing. This optimum is rather critical; if the diameter is too small, response time constants of the order of hours may result. Experimental work has been done and the results compared with theory. This work was done under ONR contract.

NOMENCLATURE

A = inside surface area of gage.
C = constant, $\frac{3}{4}[1/(2\pi RT)^{\frac{1}{2}}]\approx 10^{-5}$ sec./cm at 20°C.
L = length of tube.
p = pressure.
p_0 = pressure in system (applied at time $t=0$).
p_1 = initial pressure in gage.
p_2 = equilibrium pressure in gage.
Q = mass rate of flow.
q = surface outgassing rate.
$q' = RTq$.
R = gas constant.
r_0 = orifice radius.
r_t = tube radius.
r_{opt} = optimum tube radius.
t = time.
t_L = time constant (lag coefficient).
V = gage volume.
x = distance along tube from gage.
ρ = density.
$\varphi = r_t^3/r_0^2L$.
$\theta = r_0^{4/3}L^{5/3}/V$.

INTRODUCTION

THE reading given by a vacuum gage connected to a vacuum system by a length of tubing (see Fig. 1) does not respond immediately to a change in the pressure level in the system. There is a certain time lag during which gas molecules flow in or out of the volume of the gage and tubing until an equilibrium condition is reached (see Fig. 2). The length of this time lag depends on the geometry of the gage and tubing system, and may be of the order of hours or more unless care is taken in choosing dimensions properly. There is, in fact, an optimum size of tubing diameter for any given installation; too large a diameter increases the time lag because a larger volume must be brought into equilibrium, too small a diameter increases the time lag by increasing the resistance to flow through the tubing. In the present paper it is shown that the gage pressure varies exponentially with time, and a formula is obtained for the time constant or lag coefficient of the gage—i.e., the time within which the gage will have registered $1/e$ of its complete change following an instantaneous pressure change in the vacuum system. This formula is derived under the assumption of "free molecular flow," i.e., that the pressure level is so low that all collisions between gas molecules may be neglected. The formula has been verified experimentally and shown to be adequate for design purposes.

The equilibrium state in general results in a pressure in the gage which is different from that in the system. This is apparently due to surface outgassing or ingassing, i.e., the emission or adsorption of gas molecules at the inside surface of gage and tubing. The rate of the outgassing or ingassing also changes with time, resulting in a gage pressure change, but does so very slowly, being almost constant for hours or more. It is desirable to have an estimate of the initial equilibrium pressure difference between gage and system. Such an estimate is obtained.

RESULTS

The time constant is found to be

$$t_L = C[VL/r_t^3 + 8V/3r_0^2 + 8\pi r_t^2L/3r_0^2 + 4L^2/\pi r_t]. \quad (1)$$