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Vapour Pressure Equations for the Platinum Group Elements

IMPROVED CALCULATIONS OF VAPOUR PRESSURE AND TEMPERATURE

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While a knowledge of the vapour pressure curve of any material is of theoretical significance in understanding its basic physical properties, it can also be of practical importance in, for example, the use of the material in high-temperature vacuum applications. Therefore readily usable equations which accurately predict values of vapour pressure over a wide range of temperatures and pressures can have an important practical use. For the platinum group metals (pgms) the vapour pressures can be immediately assessed from about 10^{-16} bar to just above the boiling point by the use of Equation (i), fitted for the solid and liquid metals separately: $\ln(p, \text{bar}) = A + B\ln(T) + C/T + DT + ET^2$, *where p is the vapour pressure, T is the temperature in kelvin and A, B, C, D and E are constants. Although containing five coefficients, this equation can easily be evaluated by computers and scientific calculators. Although it gives values of vapour pressure at fixed temperatures, by a simple and rapid use of iteration values of temperature at fixed vapour pressure, temperature-dependent values of vapour pressure can also be obtained.*

Calculation of Vapour Pressure Values

Vapour pressure values are calculated from thermodynamic data following the procedure described in Appendix A. Since free energy functions are given for one bar standard-state pressure, then the vapour pressure will also be given in bars. Values for the free energy functions and the selected heats of sublimation are given in the reviews on platinum (1) and the other five pgms: palladium (2), ruthenium (3), osmium (4), rhodium (5) and iridium (6). Since the behaviour of the specific heat capacities of the solids and their effect on the free energy functions is more complicated than for the liquids, then vapour pressure values were evaluated for the solids at 25 K intervals and the melting point, and for the liquids at 50 K intervals and the melting point, so as to give approximately equal numbers of data points. In the review on platinum (1), a minimum lower temperature of 1200 K was considered. This gives a vapour pressure of about 10^{-17} bar, which is considerably below practical measurements. For the other metals, the use of rounded temperatures gives a vapour pressure between 10^{-16} and 10^{-17} bar, which was used as the lower bound.

Selection of a Vapour Pressure Equation

The derivation of the selected vapour pressure equation (Equation (i)) is described in Appendix B.

$$\ln(p, \text{bar}) = A + B\ln(T) + C/T + DT + ET^2 \qquad \text{(i)}$$

where A, B, C, D and E are constant coefficients. Equation (i) was used by Honig and Kramer (7) to represent the vapour pressures of the elements over a wide range of temperatures and pressures.

Recent Data and Their Effect on the Selected Values

Since publication of the reviews on platinum and the other metals (1–6) newer data have become available for consideration:

(a) The standard value of the atomic weight of platinum has been changed from 195.078 ± 0.002 to 195.084 ± 0.009 (8). In the review on platinum (1) the thermodynamic properties of the condensed phases were based on an atomic weight of 195.08, and the gas phase properties had been corrected using the atomic weight of 195.078. Since the change of 0.006 to the new atomic weight was from one single determination to another, it is likely that a definitive value for the atomic weight has not yet been obtained. Therefore, for consistency with the treatment of the condensed phases, the values for the gas phase have been recalculated using an atomic weight of 195.08. The effect on the tabulated values is negligible at the level of accuracy given.

(b) Two further determinations of the vapour pressure of palladium by Zaitsev, Priselkov and Nesmeyanov (9) (1267 to 1598 K) and Ferguson, Gardner and Nuth (10) (1473 to 1973 K) led to heats of sublimation of 377.3 ± 0.1 kJ mol^{-1} and 377.7 ± 0.2 kJ mol^{-1}, respectively, in excellent agreement with the selected value of 377 ± 5 kJ mol^{-1}.

(c) A number of amendments to the calculation of the thermodynamic properties of the gaseous elements from energy levels have been found to have a negligible effect on the free energy functions at the level of accuracy given in the tables in References (1–6):

  (i) For the metals other than platinum the thermodynamic properties were calculated using mainly the 1986 CODATA Fundamental Constants (11) but all values have now been recalculated using the 2006 CODATA Fundamental Constants (12).

  (ii) Joueizadeh and Johansson (13) have revised seventeen of the energy levels of ruthenium.

  (iii) Engleman *et al.* (14) have completely revised the energy levels of palladium and extended their number.

Application of the Selected Vapour Pressure Equation to the PGMs

Coefficients corresponding to the selected vapour pressure equation for both the solid and liquid pgms are given in Table I. One criterion to be met is that the calculated vapour pressures should be equal at the melting point, or more correctly the triple point which is the solid-liquid-vapour equilibrium temperature. However, because of the high resistance of the pgms to compression, then at the level of accuracy obtainable the melting points are considered to be equal to the triple points as indicated in Appendix C.

In the review on platinum (1), only the first

Table I

Coefficients in Equation (i) for the PGMs in the Solid and Liquid States

Element	Phase	Temperature range, K	*A*	*B*	*C*	*D*	*E*
Ru	Solid	1400–2606	23.31345	– 0.632925	– 78385.0	3.36362×10^{-4}	-8.85627×10^{-8}
	Liquid	2606–4600	54.00959	– 4.54744	– 80366.4	4.73549×10^{-4}	-1.54492×10^{-8}
Rh	Solid	1200–2236	45.43958	– 3.95580	– 68981.1	2.32882×10^{-3}	-2.96772×10^{-7}
	Liquid	2236–4200	38.32595	– 2.60178	– 67855.0	-5.86242×10^{-5}	4.32765×10^{-9}
Pd	Solid	850–1828	14.37701	0.270634	– 45327.0	-1.30189×10^{-3}	2.07872×10^{-7}
	Liquid	1828–3300	92.64931	– 10.78435	– 51456.6	3.94327×10^{-3}	-2.33111×10^{-7}
Os	Solid	1700–3400	26.80257	– 1.17147	– 95027.6	5.67800×10^{-4}	-6.25215×10^{-8}
	Liquid	3400–5600	44.97739	– 3.42327	– 93300.9	2.65730×10^{-4}	-5.86394×10^{-9}
Ir	Solid	1400–2719	27.23601	– 1.22965	– 81010.4	4.34895×10^{-4}	-5.80991×10^{-8}
	Liquid	2719–5000	51.13835	– 4.06675	– 83829.3	1.29129×10^{-4}	-3.77392×10^{-9}
Pt	Solid	1200–2041.3	20.55547	– 0.279512	– 68277.9	-1.49389×10^{-4}	-3.60502×10^{-8}
	Liquid	2041.3–4200	34.89596	– 2.24178	– 68166.4	4.95301×10^{-5}	8.91166×10^{-10}

three terms of Equation (i) were used, which gave an adequate representation of the vapour pressure. However, when all five terms are used to ensure precise reproducibility for all of the metals, the correlation for platinum is extraordinary. The average deviation between the thermodynamically derived vapour pressure and the result from the equation is only ± 0.0004% for both the solid and liquid, and similar results were generally obtained for the other metals as given in Table II. Even in the worst case, for solid rhodium, agreement is still within five significant figures; this tolerance is well beyond that of any practical determination of vapour pressure.

Table II

Percentage Deviations between Thermodynamically Derived Vapour Pressure Curves and Results from Equation (i) for PGMs in the Solid and Liquid States

Element	Phase	Accuracy of fit, %
Ru	Solid Liquid	0.0014 0.0001
Rh	Solid Liquid	0.0059 0.0002
Pd	Solid Liquid	0.0020 0.0014
Os	Solid Liquid	0.0008 0.0000
Ir	Solid Liquid	0.0002 0.0003
Pt	Solid Liquid	0.0004 0.0004

Whereas the equations for the liquids reproduce the thermodynamic boiling points to within 0.01 K, more realistic estimates of the uncertainties in the boiling points can be ascertained from the uncertainties assigned to the enthalpies of sublimation, with boiling point uncertainties rounded to the nearest 10 K (see Table III).

The uncertainties given in Table III must be considered to be minimum values, because the uncertainties in the free energy functions are not taken into account. For example, the enthalpy of fusion and thermodynamic properties of liquid osmium are all estimated, and therefore a more realistic estimate of the uncertainty in the boiling point would be ± 100 K.

Table III

Uncertainties in the Boiling Points of PGMs

Element	Enthalpy of sublimation ± uncertainty $\Delta H^\circ_{298.15}$, kJ mol^{-1}	Boiling point ± uncertainty T, K
Ru	649 ± 4	4592 ± 30
Rh	558 ± 10	4114 ± 90
Pd	377 ± 5	3263 ± 50
Os	788 ± 4	5576 ± 30
Ir	670 ± 6	4898 ± 50
Pt	565 ± 2	4149 ± 20

Temperatures Corresponding to Given Vapour Pressures

These values are given in Table IV. Since the lowest temperature used corresponds to a vapour pressure between 10^{-17} and 10^{-16} bar, then 10^{-16} bar is used as the lower bound for fixed pressures. Table IV provides a check on values obtained by iteration of the equations. It is an amendment to a previous summary (15), in which the lowest pressure included was 10^{-12} bar. Vapour pressures corresponding to fixed temperatures are obtained directly from the equations, and a check is provided by Table V, which lists the melting point vapour pressures.

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Table IV

Temperatures Corresponding to Fixed Vapour Pressures for the PGMs

Pressure	Temperature, K					
p, bar	Ru	Rh	Pd	Os	Ir	Pt
10^{-16}	1403	1219	870	1706	1456	1238
10^{-15}	1464	1273	911	1780	1520	1292
10^{-14}	1530	1332	956	1861	1590	1352
10^{-13}	1603	1396	1005	1950	1667	1417
10^{-12}	1684	1468	1060	2048	1751	1489
10^{-11}	1772	1546	1122	2156	1844	1569
10^{-10}	1871	1634	1191	2277	1949	1659
10^{-9}	1982	1733	1269	2411	2065	1759
10^{-8}	2107	1845	1359	2563	2197	1872
10^{-7}	2249	1972	1462	2736	2347	2002
10^{-6}	2412	2119	1582	2934	2520	*2156*
10^{-5}	2602	*2293*	1725	3163	*2721*	*2339*
10^{-4}	*2842*	*2508*	*1899*	*3435*	*2976*	*2558*
10^{-3}	*3134*	*2772*	*2120*	*3793*	*3288*	*2824*
10^{-2}	*3498*	*3102*	*2400*	*4239*	*3681*	*3155*
10^{1}	*3965*	*3530*	*2765*	*4810*	*4193*	*3580*
1	*4588*	*4110*	*3259*	*5571*	*4894*	*4146*
NBP*	*4592*	*4114*	*3263*	*5576*	*4898*	*4149*

**NBP = normal boiling point at one atmosphere pressure (1.01325 bar)*
Values corresponding to the liquid region are given in italics

Table V

Vapour Pressures at the Melting Points for the PGMs

Element	Melting point *T*, K	Vapour pressure *p*, bar
Ru	2606	1.045×10^{-5}
Rh	2236	5.050×10^{-6}
Pd	1828.0	4.227×10^{-5}
Os	3400	7.753×10^{-5}
Ir	2719	9.837×10^{-6}
Pt	2041.3	1.896×10^{-7}

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Appendix A

Calculation of Vapour Pressure Values

Vapour pressure values may be calculated from thermodynamic data *via* an inversion of the third law of thermodynamics used to calculate the heat of sublimation (Equation (ii)):

$$RT\ln(p) = T[\delta - (G^\circ_T - H^\circ_{298.15})/T] - \Delta H^\circ_{298.15(\mathrm{III})} \qquad \text{(ii)}$$

where R is the universal gas constant (8.314472 J mol^{-1} K^{-1} (12)); T is the temperature in kelvin; p is the vapour pressure in bar; $\Delta H^\circ_{298.15(\mathrm{III})}$ is the third law enthalpy of sublimation at 298.15 K (Equation (iii));

$$\delta - (G^\circ_T - H^\circ_{298.15})/T = [-(G^\circ_T - H^\circ_{298.15})/T_{(\mathrm{g})}] - [-(G^\circ_T - H^\circ_{298.15})/T_{(\mathrm{s,\,l})}] \qquad \text{(iii)}$$

where $(G^\circ_T - H^\circ_{298.15})$ is the free energy of the phase relative to that at 298.15 K.

Appendix B

Derivation of the Selected Vapour Pressure Equation

The variation of vapour pressure (p) with temperature (T) can be represented by the Clapeyron equation (Equation (iv)):

$$\mathrm{d}p/\mathrm{d}T = \Delta H/T\Delta V \qquad \text{(iv)}$$

where ΔH is the latent heat of sublimation (below the melting point) or vaporisation (above the melting point); ΔV is the change in volume during the transition from condensed phase to gas. Since the volume change is very large, the value for the condensed phase can be neglected and the equation becomes Equation (v) or (vi):

$$\mathrm{d}p/\mathrm{d}T = \Delta Hp/RT^2 \qquad \text{(v)}$$

$$\mathrm{d}\ln(p)/\mathrm{d}T = \Delta H/RT^2 \qquad \text{(vi)}$$

Equation (vi) is then integrated to give the Clausius-Clapeyron equation (Equation (vii)):

$$\ln(p) = A/T + B \qquad \text{(vii)}$$

where B is an integration constant, and $A = \Delta H_T/R$ where ΔH_T is the average enthalpy centred on the mid-range temperature; ΔH_T can only be taken as constant over a relatively narrow temperature range. The Clausius-Clapeyron equation is used practically to fit experimental vapour pressure measurements, and also to calculate the 'second law' heat of sublimation through the relationship (Equation (viii)):

$$\Delta H^\circ_{298.15(\mathrm{II})} = -\delta(H^\circ_T - H^\circ_{298.15}) - RA \qquad \text{(viii)}$$

where $\delta(H^\circ_T - H^\circ_{298.15})$ and $(H^\circ_T - H^\circ_{298.15})$ (see Equation (ix)) are enthalpy values relative to the enthalpy at 298.15 K;

$$\delta(H^\circ_T - H^\circ_{298.15}) = (H^\circ_T - H^\circ_{298.15})_{(g)} - (H^\circ_T - H^\circ_{298.15})_{(s,\,l)} \qquad \text{(ix)}$$

ΔH_T may be taken as constant only for a narrow temperature range. In order to cover a wider temperature range it may be expanded to Equation (x):

$$\Delta H_T = \Delta H_0 + a_1 T + a_2 T^2 + a_3 T^3 + \ldots \qquad \text{(x)}$$

Substituting Equation (x) into the Clapeyron equation (Equation (iv)) gives Equation (xi):

$$\mathrm{d}\ln(p) = \Delta H_0 \mathrm{d}T/RT^2 + a_1 \mathrm{d}T/RT + a_2 \mathrm{d}T/R + a_3 T\mathrm{d}T/R \qquad \text{(xi)}$$

Rearranging the coefficients and integrating gives Equation (xii):

$$\ln(p) = A + a_1 \ln(T)/R - \Delta H_0/RT + a_2 T/R + a_3 T^2/R \qquad \text{(xii)}$$

where A is the integration constant. Substituting $B = a_1/R$, $C = -\Delta H_0/R$, $D = a_2/R$, $E = a_3/R$ gives Equation (i):

$$\ln(p, \text{bar}) = A + B\ln(T) + C/T + DT + ET^2 \qquad \text{(i)}$$

Appendix C

Melting Point and Triple Point Differences

Although the pressure at the standard state in thermodynamics is now set at one bar, melting points are still quoted at one atmosphere pressure. This is an arbitrary choice, whereas the triple point is that at which the vapour pressures of the solid, liquid and gas are exactly equal; it is therefore a universal point. The difference between the melting and triple points can be determined from the melting pressure curves, for example Strong and Bundy (16) determined the initial values for these curves to be 138 atm deg^{-1} for platinum and 160 atm deg^{-1} for rhodium, equivalent to 0.007 deg atm^{-1} and 0.006 deg atm^{-1}, respectively. Assuming that the triple point pressures are equal to zero, then this indicates that for platinum, the triple point would be 0.007 K below the melting point, and for rhodium 0.006 K. However, these values are negligible when compared to melting point uncertainties of ± 0.4 K for platinum and ± 3 K for rhodium at the secondary fixed points on the International Temperature Scale of 1990 (ITS-90) (17). On these grounds, triple point corrections may be regarded as meaningless. These examples for platinum and rhodium are considered as representative for all six of the pgms.

The Author

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