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J. P. Chan and Ralph Hultgren

June 1968

The Thermodynamic Properties of Silver-Palladium Alloys

By

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Abstract

Heats of formation of silver-palladium solid solutions were measured by liquid tin solution calorimetry. The maximum exothermic heat of formation was found to lie at 40 atomic percent palladium. This was correlated with the magnetic character of the alloys; they are diamagnetic below 40 atomic percent palladium and paramagnetic above. Pauling's theory of metallic chemical bonding provides a satisfactory explanation of this.

Introduction. The alloy chemistry of transition metals is poorly understood, both because of lack of thermodynamic data and because of the complexity of electronic structure of these metals. The silver-palladium system was chosen for study because relatively simple bonding concepts lead to a prediction that the exothermic heat of formation should be greater on the silver-rich side, reaching a maximum near 40 atomic percent palladium. This was

found to be the case.

Transition metals are characterized by having incompletely filled inner d-orbitals; the resulting unpaired electrons make these metals paramagnetic or ferromagnetic. Palladium has approximately 0.6 unpaired electrons per atom. Silver has one more electron than palladium (the atomic number is one greater); this is more than sufficient to fill all the d-orbitals so that silver is diamagnetic, with 0.4 excess electrons per atom in higher energy levels.

Silver and palladium form a complete series of face-centered-cubic solid solutions. Substitution of a silver atom for a palladium atom on the crystal lattice increases the number of electrons by one. On the palladium-rich side, the extra electron enters the d-orbital, reducing the paramagnetic susceptibility. When the silver concentration reaches 60 atomic percent, all the d-orbitals are filled and alloy becomes diamagnetic. Further increases in silver concentration produce a change in bonding electron density with an effect on the heat of formation of the alloy which differs from that on the palladium-rich side. The magnetic susceptibilities^{1, 2, 3} shown in Figure 1 confirm this description.

Experimental. Palladium sponge 99.99% pure and electrolytic silver 99.95% pure were used to make the alloys. Mixtures of filings in zirconia lined graphite crucibles were melted at about 1500°C under helium by induction heating to make ingots weighing about 3 grams each. After cold-working, the ingots were sealed in evacuated quartz tubes and homogenized by heating

for two to three weeks at temperatures 50-100° below the solidus (1000°C to 1300°C). Homogeneity was tested by X-ray diffraction of mixtures of filings taken from both ends of each ingot, after strain-annealing the filings at 600°C for thirty minutes in evacuated Pyrex glass tubes. Back-reflection lines were sharp and the lattice constants agreed well with those of Coles⁴ for the expected compositions, assuming small losses of silver during melting.

Heats of formation of the alloys were determined in a liquid-tin solution calorimeter described elsewhere⁵. In this method the heat of solution of the alloy is subtracted from the heats of solution of corresponding amounts of the pure components, to give the heat of formation of the alloy. Experimental data are given in Table I.

The heat contents of the alloys were measured in a diphenyl ether drop calorimeter⁶. The experimental results are given in Table II. A moderate negative deviation from additivity of heat contents was found. From the heat contents the heats of formation, which were measured near room temperature, can be calculated at high temperatures.

The heats of solution of silver and palladium in liquid tin, calculated at 700°K are shown in Table III. The heats of formation of the alloys, calculated at 1200°K are shown in Table IV.

Discussion. The extraordinarily high exothermic heat of solution of palladium in tin is surprising. None of the generalizations on metallic bonding give a hint that palladium would differ much from silver. Palladium and silver have atomic radii (1.375 and 1.445Å) which differ by only 5% and their

electronegativities are also not very different (2.2 and 1.9). Yet palladium has one of the most exothermic heats of solution known, while silver dissolves endothermically. Silver and palladium, as shown in this paper, behave normally to one another, forming alloys with moderate exothermic heats. Clearly there are large factors in the formation of metallic bonds in alloys which are not explainable on the simple concepts of electronegativity and atomic size.

The heats of formation at 1200°K of silver-palladium alloys are shown in Figure 2. Their dependence on concentration resembles a parabola, such as would be predicted by the well-known quasi-chemical theory in which heats of formation depend on the number of bonds between unlike nearest neighbors, except that they are strongly skewed toward the silver-rich side. The maximum exothermic effect occurs near 40 atomic percent palladium; significantly, this is the composition where magnetic properties drastically change (Figure 1), the alloys are diamagnetic at lower palladium contents, and paramagnetic at higher.

This behavior is not peculiar to silver-palladium alloys. It seems to appear in all binary alloys where one metal is from the Ni-Pd-Pt column of the periodic table and the other member is from the Cu-Ag-Au column. Thus, besides Ag-Pd, Cu-Pd⁷, Au-Pd⁸, Cu-Pt⁹, are exothermic, skewed toward the Cu-rich or Au-rich side, with maximum exothermic effect near 40 atomic percent Pd or Pt. Cu-Ni¹⁰ and Au-Ni¹¹ are endothermic, but are less endothermic on the Cu-rich or Au-rich sides. Ag-Ni¹², Ag-Pt¹², and

Au-Pt¹² have miscibility gaps; the first is highly immiscible even in the liquid state, the latter two are more miscible at the Ag-rich and Au-rich sides, respectively. Thus of the nine binary combinations, none disagree with the observation that the exothermic character is greater on the Cu-, Ag-, or Au-rich sides of the binary alloys.

Pauling's theory of metallic bonding agrees nicely with this result. According to Pauling¹³ the transition metals in the middle of the periodic table, including palladium develop a valence of 6 in the metallic state. Silver, however, is hyperelectronic; the electrons in excess of those necessary to fill the d-orbital are paired with electrons which would otherwise be valence electrons. Thus silver, with 0.4 excess electrons, develops a valence of only 5.6 (or 5.56). Each Pd atom which enters the Ag lattice removes an excess electron into its incompletely filled d-orbital increasing the valence of the Ag; when x_{Pd} reaches 0.40, the valence of the remaining silver atoms reaches 6.0. Thus on the Ag-rich side of the phase diagram each Pd atom increases the valence, contributing to the exothermic character of the alloy; this ceases as the concentration of Pd exceeds 40 atomic percent. The valence is shown graphically in Figure 3, with the extra valence contribution shown in the shaded area.

Myles¹⁴ has recently determined Gibbs energies of Ag-Pd solid solutions from vapor pressure measurements. Combining these values with the enthalpies of formation determined in this paper, the ΔS values shown in Table IV and Figure 2 are obtained.

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TABLE I

Measured Heats of Solution and Heats of Formation of the Alloys

X_{Pd}	$T_i, ^\circ K$	$T_f, ^\circ K$	$\Delta H_{sol'n}$ cal/g-atom	$\Delta H_{formation}$ cal/g-atom
1.000	342.7	700.8	-23900	
1.000	342.6	700.8	-24210	
0.798	324.6	703.2	-17430	-410
0.798	343.0	701.5	-17440	-510
0.612	324.9	701.4	-11240	-990
0.612	343.1	700.7	-11320	-1030
0.492	324.8	700.8	-7470	-1150
0.492	342.4	700.5	-7580	-1150
0.394	324.9	699.6	-4380	-1290
0.394	326.1	706.6	-4400	-1230
0.200	324.6	698.4	1130	-950
0.200	342.8	700.2	1010	-930
0.000	325.6	699.1	6150	
0.000	325.9	705.2	6300	
0.000	342.9	699.2	6120	
0.000	342.6	699.2	6090	

TABLE II

Measured Heat Contents for the Alloys

X_{Pd}	T, °K	$H_T - H_{298.15}$ cal/g-atom	$\Delta(H_T - H_{298.15})$ cal/g-atom
0.200	998.3	4560	-40
0.200	1021.5	4670	-90
0.200	1076.4	5040	-120
0.200	1078.7	5050	-130
0.394	989.4	4440	-110
0.394	1095.4	5240	-80
0.394	1095.7	5260	-60
0.492	892.9	3820	-60
0.492	998.6	4530	-100
0.492	1078.2	5210	0
0.798	886.8	3880	10
0.798	998.9	4670	0
0.798	1021.3	4770	-60

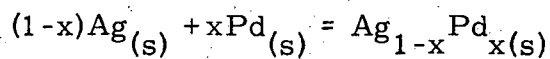
TABLE III

Measured Heats of Solution in Tin at 700°K for Pure Silver and Palladium

Substance	$\Delta H_{\text{sol'n}} 700^\circ\text{K}$ cal/g-atom
Pd	-26400±160
Ag	3845±55

TABLE IV

Silver-Palladium Alloys at 1200°K



X_{Pd}	ΔG	ΔH	ΔS
0.1	-1196	-725	0.392
0.2	-1927	-1115	0.677
0.3	-2318	-1320	0.832
0.4	-2429	-1370	0.882
0.5	-2327	-1300	0.856
0.6	-2087	-1110	0.814
0.7	-1751	-850	0.751
0.8	-1338	-590	0.623
0.9	-825	-310	0.429

References

1. B. Svensson, Ann. Phys. Lpz., 14, 699 (1932).
2. J. Wucher, Thesis, Strassbourg (1950).
3. F.E. Hoare, J.C. Mathews, and J.C. Walling, Proc. Roy. Soc., 216, 502 (1953).
4. B.R. Coles, J. Inst. Metals, 84, 346 (1956).
5. R.L. Orr, A. Goldberg, and R. Hultgren, Rev. Sci. Instr., 28, 767 (1957).

6. R. Hultgren, P. Newcombe, R. L. Orr, and L. Warner, National Physical Laboratory, Symposium No. 9, 1959, H. M. S. O., London, Paper No. 14.
7. J. R. Guadagno, R. L. Orr, and R. Hultgren, 13th Tech. Report, Minerals Research Lab., Berkeley (Sept. 1, 1961).
8. J. B. Darby, Jr., Acta Met. 14, 265 (1966).
9. K. M. Myles and J. B. Darby, Jr., Acta Met., 16, 485 (1968).
10. R. Oriani, and W. K. Murphy, Acta Met., 8, 23 (1960).
11. R. L. Orr, Acta Met., 8, 489 (1960).
12. M. Hansen, "Constitution of Binary Alloys", McGraw Hill, 1958.
13. L. Pauling, "Nature of the Chemical Bond", Cornell Univ. Press, 3rd Ed., 1960.
14. K. M. Myles, Acta. Met., 13, 109 (1965).

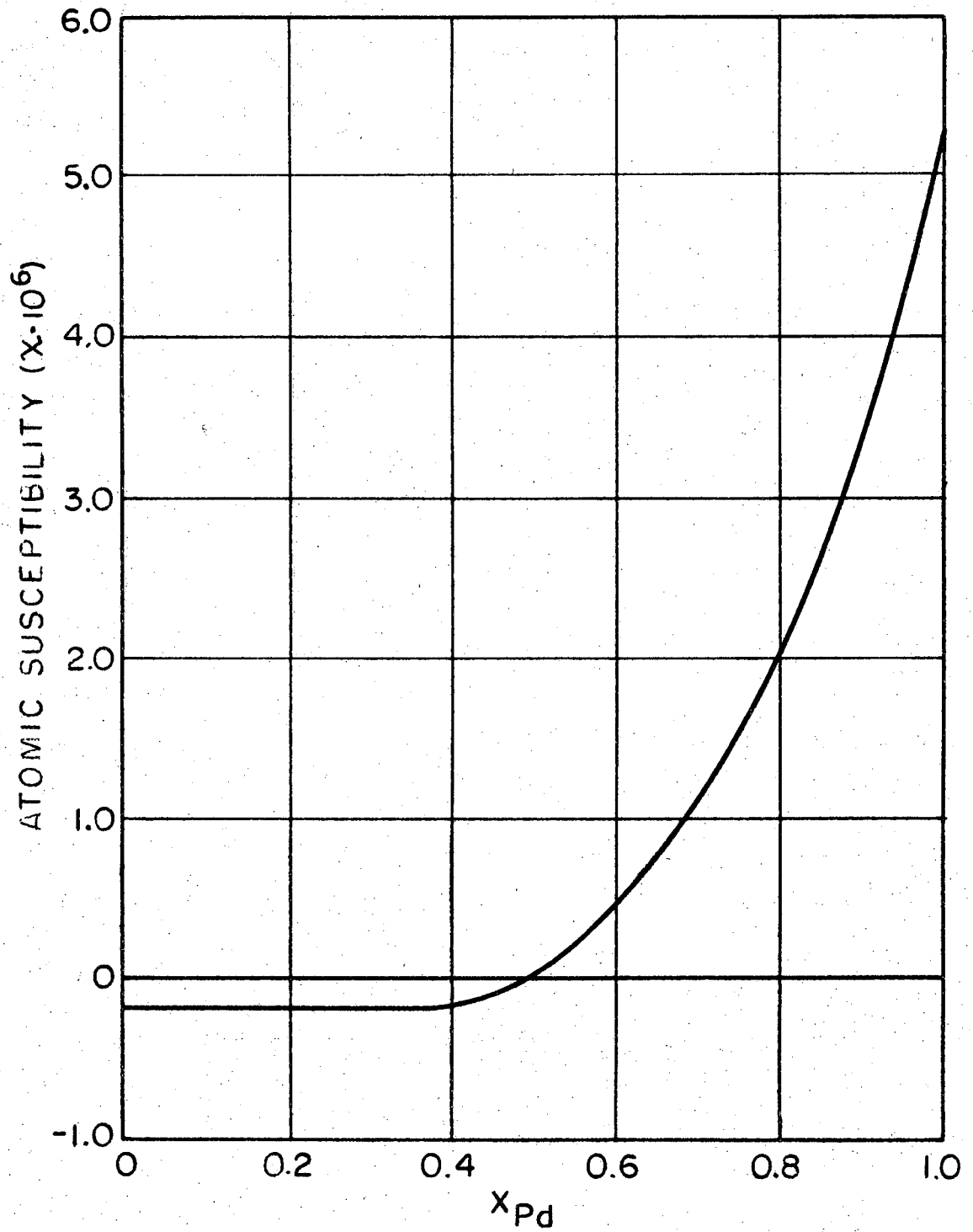


Figure 1. Magnetic Susceptibility versus Composition for Silver-Palladium Alloys at 20°C.

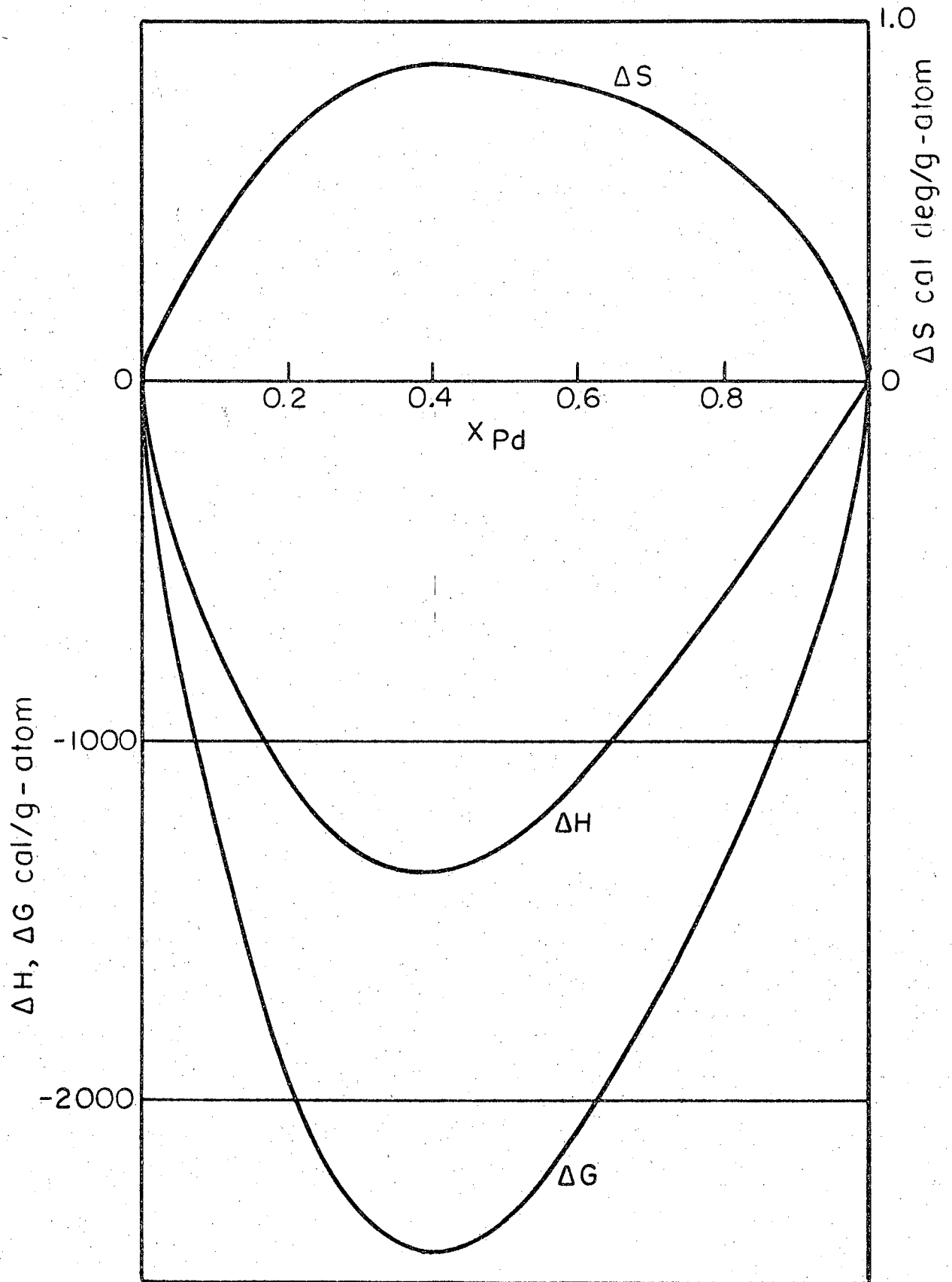


Figure 2. Thermodynamic Properties of Silver-Palladium Alloys at 1200°K.

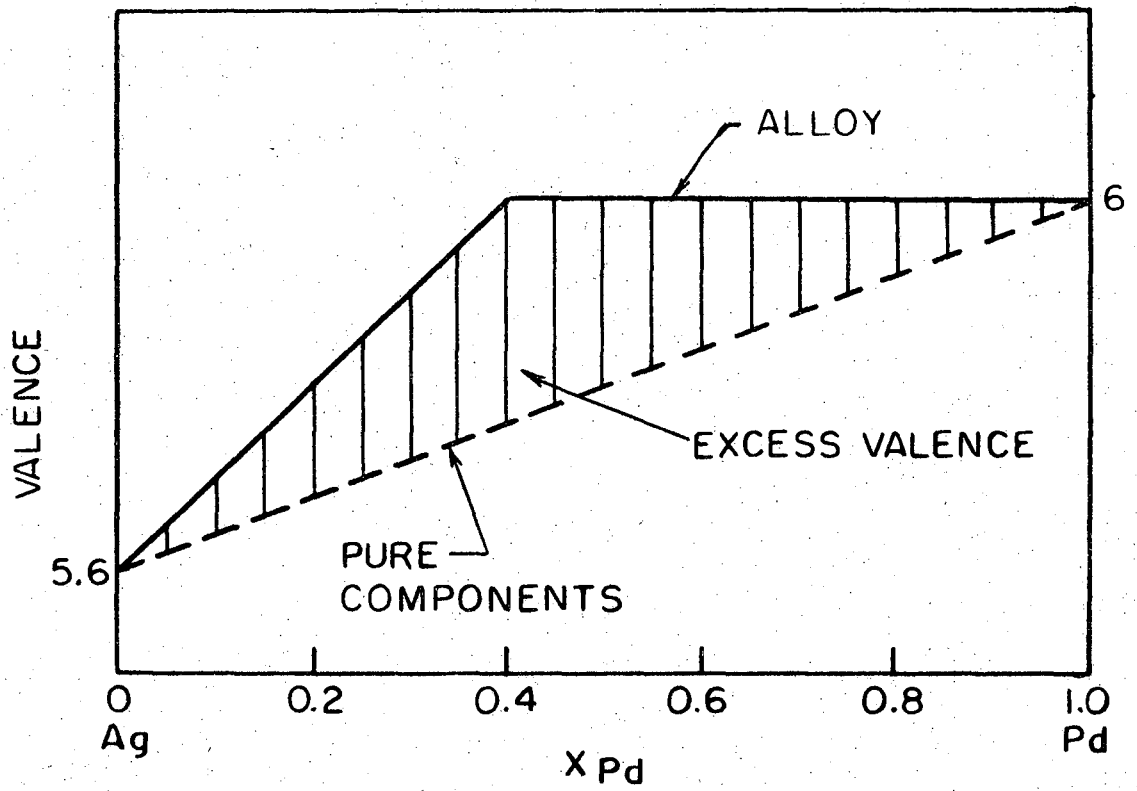


Figure 3. Metallic Valences from Pauling's Theory.

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