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Running title: Assessing the high concentration of vacancies in refractory high entropy alloys

SUPPLEMENTARY INFORMATION

Supplementary Figures:

Supplementary Tables:

Supplementary Appendices:

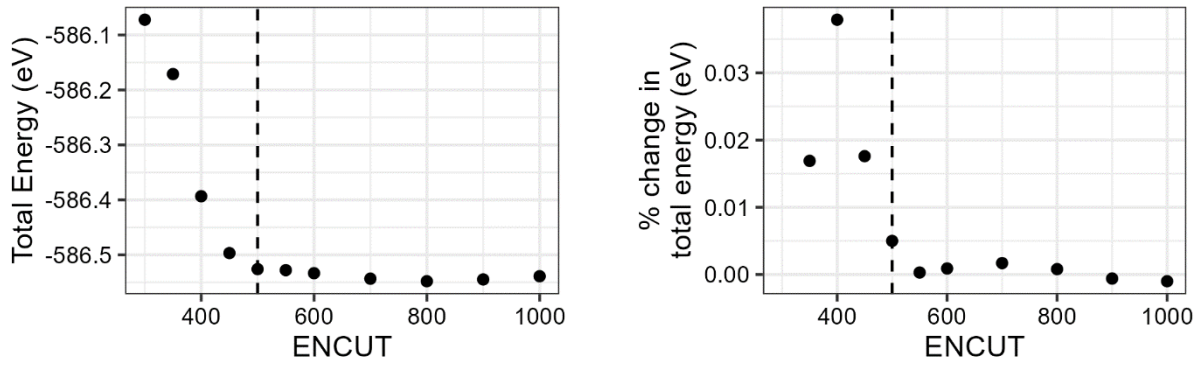

Figure S1. ENCUT convergence testing. Convergence testing for ENCUT values (the plane wave cut-off

energy) for a 54-atom body-centred $Mo_{11}Nb_{11}Ta_{11}Ti_{10}W_{11}$ supercell. An ENCUT value (dashed vertical line) was chosen for which an increase of 50 eV resulted in less than 0.01 % change in total energy. **(Left)** Total energy plotted against ENCUT value. **(Right)** Percentage change in total energy plotted against ENCUT.

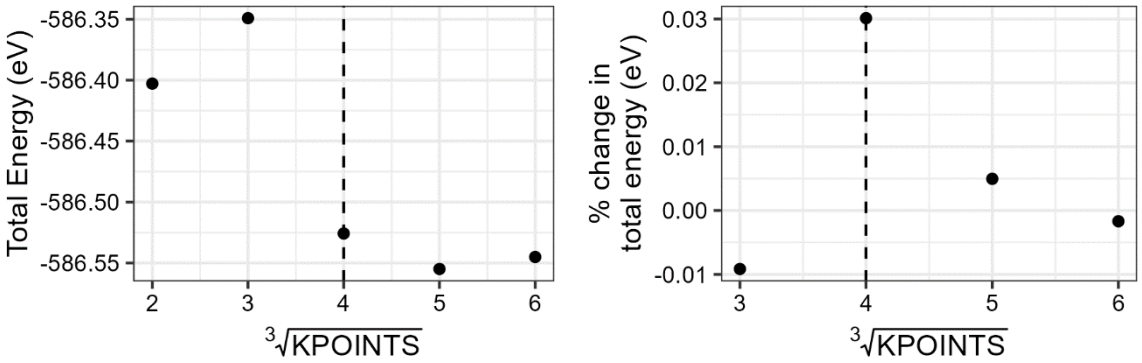

Figure S2. KPOINTS convergence testing. Convergence testing for number of KPOINTS of a 54-atom body-centred $Mo_{11}Nb_{11}Ta_{11}Ti_{10}W_{11}$ supercell. A KPOINTS set (dashed vertical line) was chosen for which a further increase of KPOINTS resulted in less than 0.01 % change in total energy. **(Left)** Total energy plotted against ENCUT value. **(Right)** Percentage change in total energy plotted against number of KPOINTS.

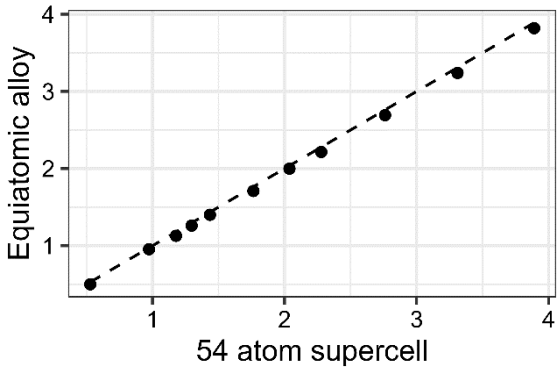

Figure S3. Effect of the equiatomic approximation in calculating local element bias. $\mathrm{R}^2 = 1.00$. Local element bias is calculated using equation 1 on a range of local vacancy environments listed in **Table S1** for an equiatomic quinary alloy and a 54 atom supercell (comprising elements A-E; A-D: 11 atoms and E: 10 atoms). A dashed line indicates the function $y = x$.

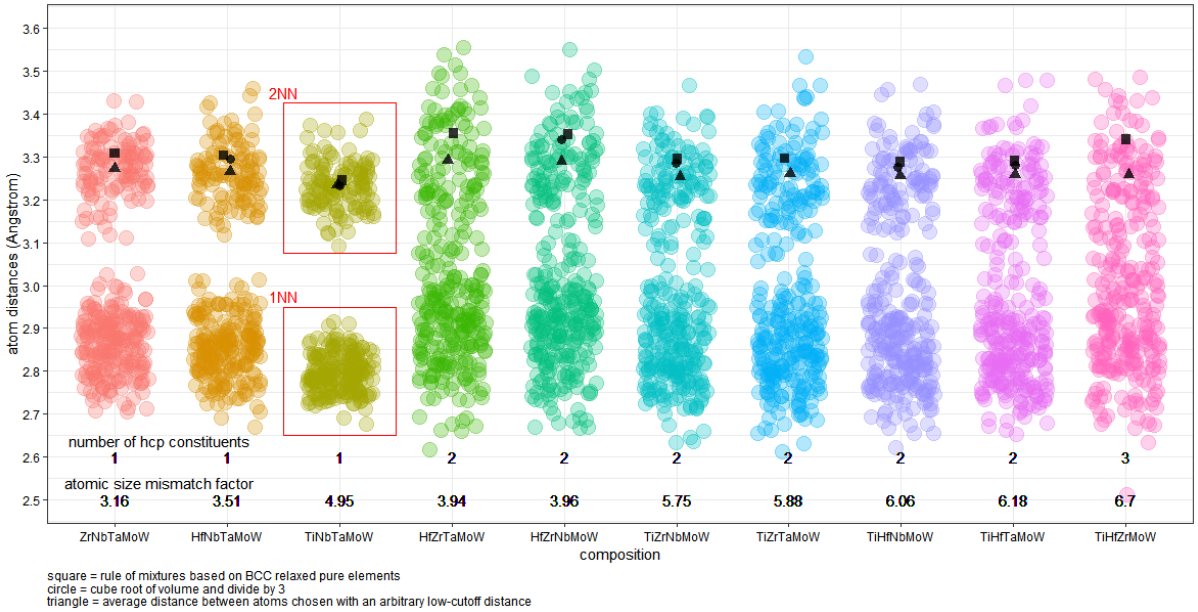

Figure S4. Atomic distances in solid solutions. Atomic distances of quinary alloys in the Hf-Mo-Nb-Ta-Ti-W-Zr system. The rule of mixtures ignores any enthalpic contributions or lattice distortions so is likely to overpredict lattice parameters. Taking the mean of the second nearest neighbour distances is likely to underpredict the lattice parameter in some cases when its distribution overlaps with the first nearest neighbours. It is thought that the most representative method is to cube-root the volume and divide by three, although this does lose information about the spread of atomic distances in the actual supercell. Method A is believed to produce the most representative lattice parameter found in bulk materials. Method B generally results in inaccurate results in cases where the overlap between 1NN and 2NN distances becomes significant (E.g., in TiHfZrMoW). Method C (Vegard's law) generally produced larger lattice parameters due to neglecting lattice strain on structure relaxation. The lattice constants for fully relaxed body-centred cubic supercells of pure elements used for Method C, are Ti: 3.25; Zr: 3.57; Nb: 3.31; Mo: 3.16; Hf: 3.54; Ta: 3.32; and W: 3.18 Å.

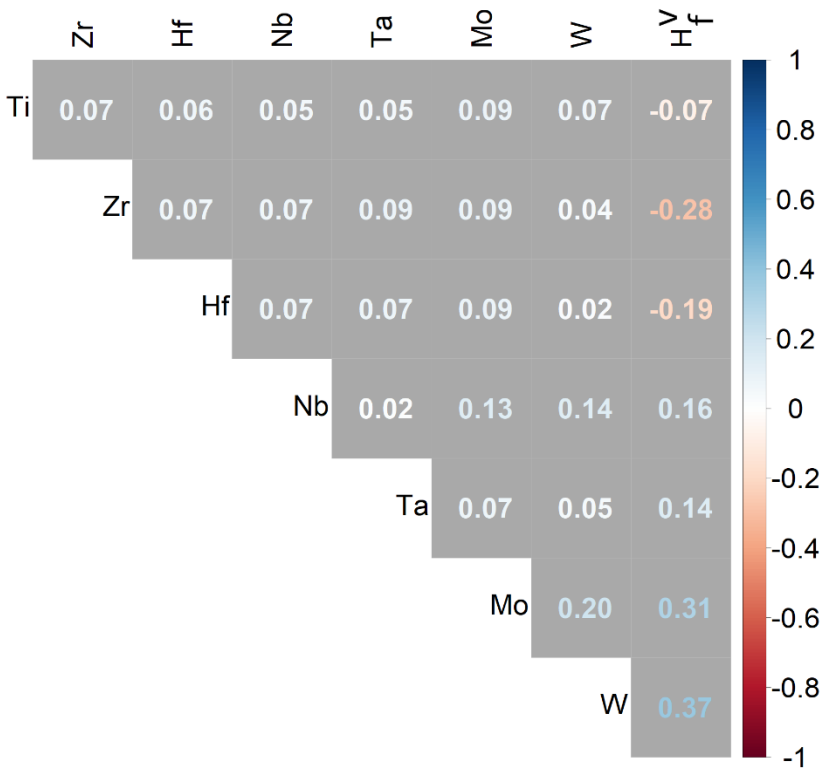

Figure S5. Product-moment correlation coefficient between nearest neighbour atoms (< 2.75 Å) and the calculated vacancy formation enthalpy, H_f^v.

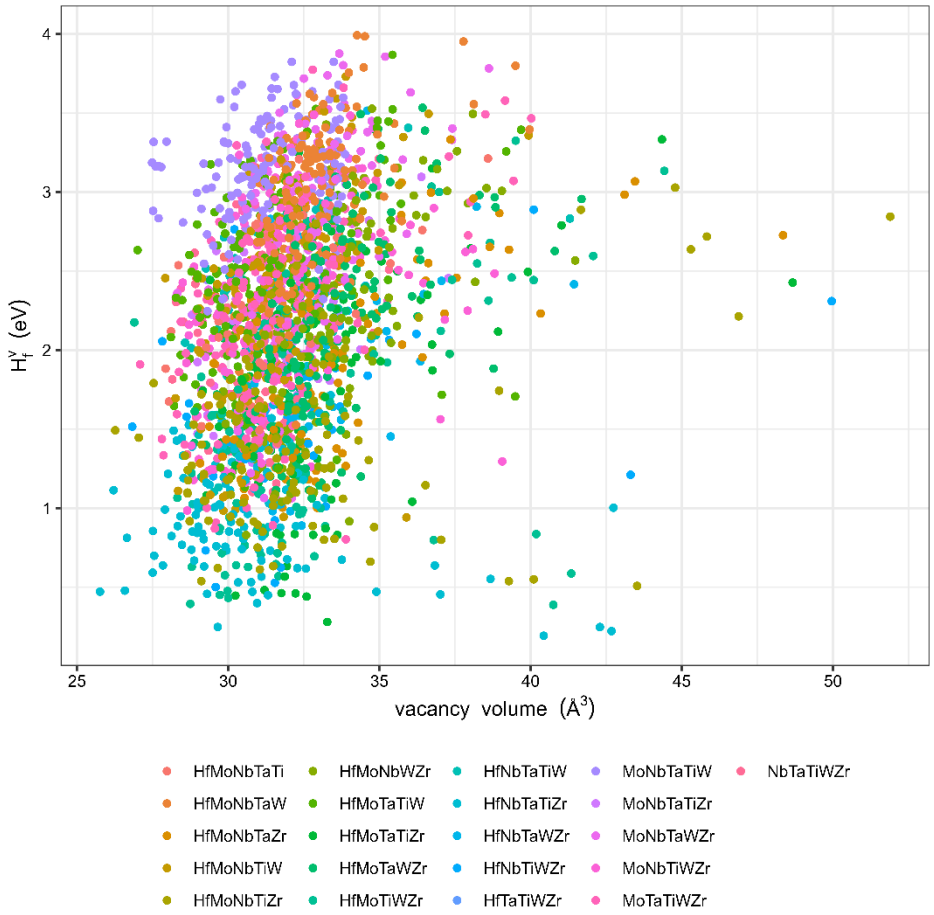

Figure S6. Enthalpy of vacancy formation, H_f^v, versus vacancy volume. $r = +0.28$.

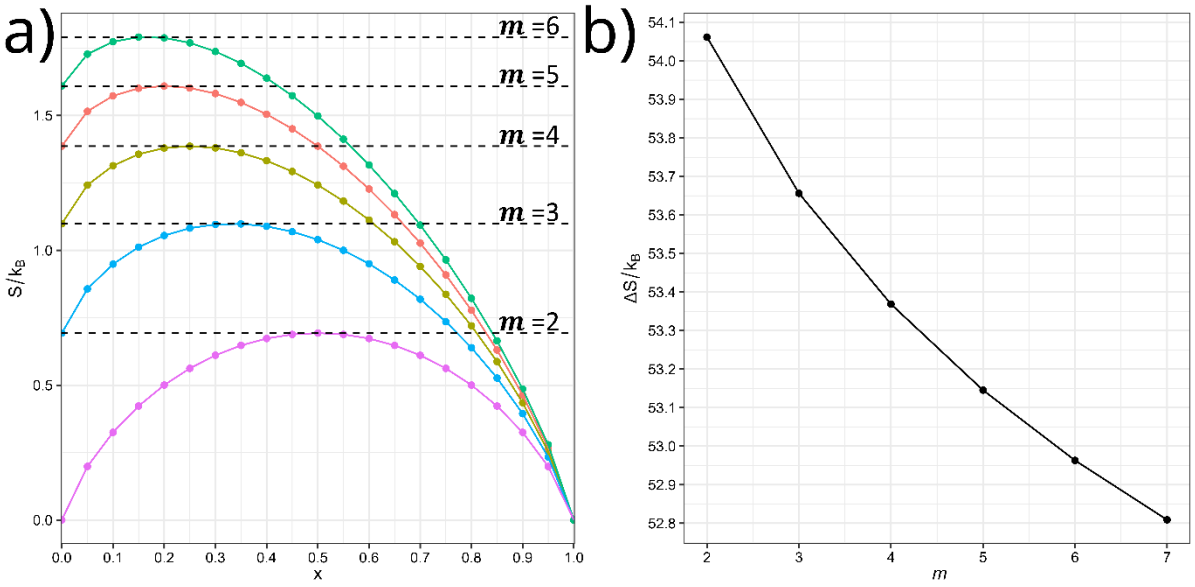

Figure S7. Configurational entropy in the $m + 1$ scheme. Where x is the mol% of an element in an alloy, m is the alloying number, and K_b is the Boltzmann constant; a) configurational entropy for alloys up to the senary alloy; b) configurational entropy of an added vacancy to an m-element alloy.

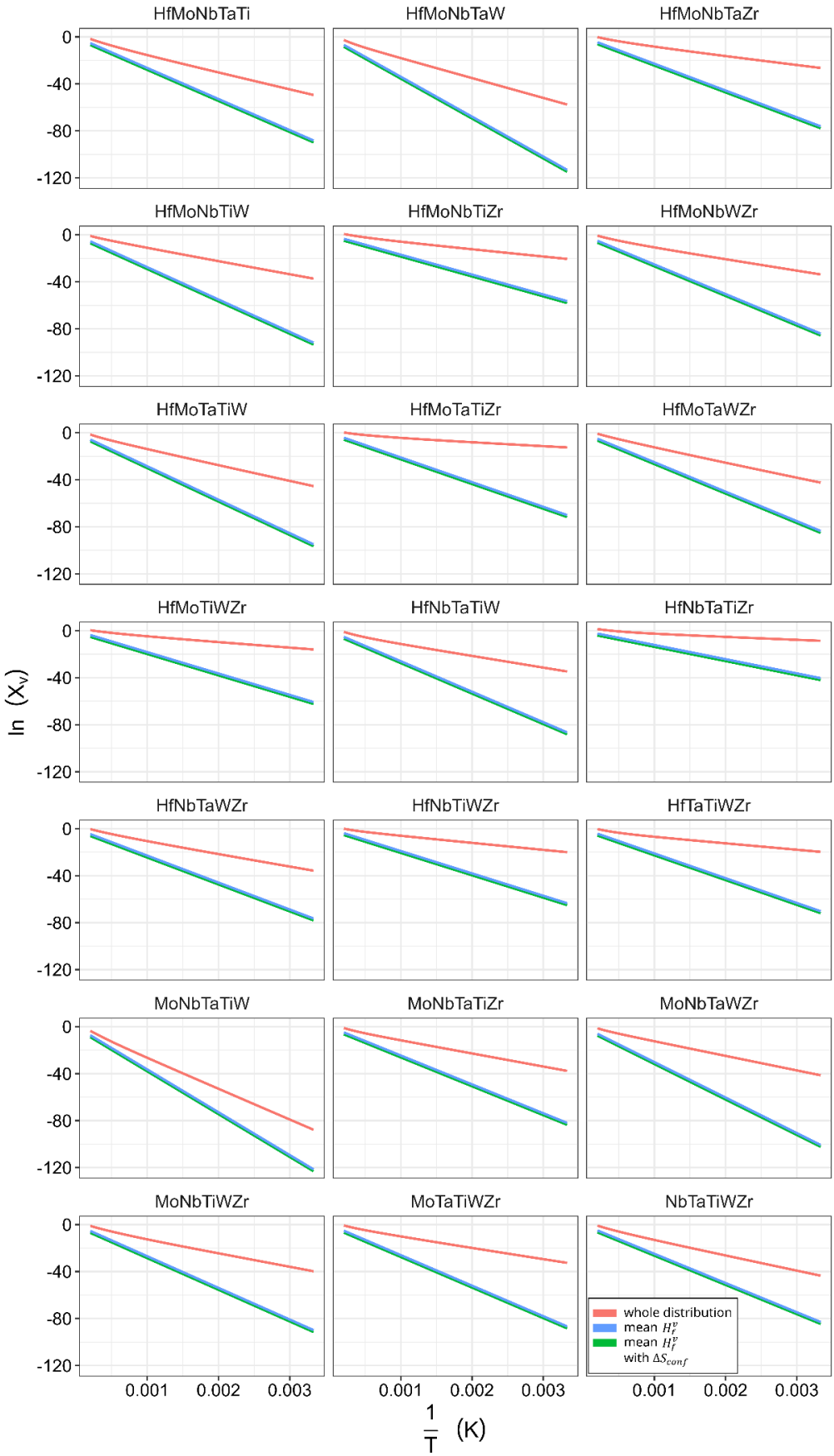

Figure S8. Vacancy population versus reciprocal temperature. X_v is the equilibrium vacancy concentration, $X_v = \frac{n}{N}$.

Table S1. Example calculations of local element bias. Local element biases calculated around vacancy defects in equiatomic quinary body-centred cubic alloys via **equation 1**.

Number of each element A-E					Local element bias
A	B	C	D	E	
2	2	2	1	1	1.04
2	2	2	2	0	1.75
3	2	2	1	0	1.91
3	3	1	1	0	2.37
3	3	2	0	0	2.76
4	3	1	0	0	2.93
4	4	0	0	0	3.82
5	3	0	0	0	3.46
6	2	0	0	0	3.42
7	1	0	0	0	3.72
8	0	0	0	0	4.29

Table S2. Two-tailed Kolmogorov–Smirnov test on the vacancy formation enthalpies produced by multiple special quasi-random structures. D indicates the test statistic. p indicates the p-value of the test. A-C indicates the series of SQS cells calculated and is unique between each composition.

composition	D (A-B)	p (A-B)	D (A-C)	p (A-C)	D (B-C)	p (B-C)
HfMoNbTaTi	0.148	0.598	NA	NA	NA	NA
HfMoNbTaW	0.148	0.598	0.13	0.76	0.148	0.598
HfMoNbTaZr	0.278	0.031	0.241	0.087	0.204	0.214
HfMoNbTiW	0.13	0.76	0.148	0.598	0.13	0.76
HfMoNbTiZr	0.222	0.139	0.093	0.977	0.259	0.053
HfMoNbWZr	0.093	0.977	0.167	0.445	0.111	0.897
HfMoTaTiW	0.111	0.897	0.148	0.598	0.185	0.315
HfMoTaTiZr	0.259	0.053	0.185	0.315	0.185	0.315
HfMoTaWZr	0.241	0.087	0.185	0.315	0.13	0.76
HfMoTiWZr	0.204	0.214	NA	NA	NA	NA
HfNbTaTiW	0.167	0.445	0.185	0.315	0.111	0.897
HfNbTaTiZr	0.204	0.214	0.259	0.053	0.315	0.009
HfNbTaWZr	0.204	0.214	0.148	0.598	0.222	0.139
HfNbTiWZr	0.148	0.598	NA	NA	NA	NA
HfTaTiWZr	0.259	0.053	NA	NA	NA	NA
MoNbTaTiW	0.074	0.999	0.074	0.999	0.019	1
MoNbTaTiZr	0.111	0.897	NA	NA	NA	NA
MoNbTaWZr	0.167	0.445	0.204	0.214	0.333	0.005
MoNbTiWZr	0.278	0.031	0.111	0.897	0.259	0.053
MoTaTiWZr	0.204	0.214	0.204	0.214	0.167	0.445
NbTaTiWZr	0.185	0.315	0.167	0.445	0.111	0.897

Appendix S1

Beginning from the Gibbs energy to form a vacancy:

$$\Delta \mathrm{G} = \Delta \mathrm{H} - \mathrm{T}\Delta S$$

where $\Delta \mathrm{G}$ is the Gibbs free energy to form a vacancy, $\Delta \mathrm{H}$ is the associated enthalpy of formation for a vacancy and is assumed to be invariant with temperature, ΔS is the entropy of a vacancy, which is assumed to be dominated by the configurational entropy. All units of energy are in electron volts. The configurational entropy is given by Boltzmann's famous equation, $\mathrm{S_{conf}} = \mathrm{k_B ln}(\Omega)$. Here, $\mathrm{k_B}$ is the Boltzmann constant in $(\mathrm{eVK^{-1}})$ and Ω is the possible number of microstates in the system. The number of possible microstates for an m-element alloy with vacancies is given by

$$\mathrm{S} = \mathrm{k_B ln}\left[\frac{N!}{N_A!\, N_B!\, N_C!\, N_D!\, N_E!\ \ldots\ n!}\right]$$

where N is the total number of atoms in the system, N_{A-E} is the number of atoms of element A–E, respectively, and n is the number of vacancies in the alloy. Assuming that the alloy is equiatomic (i.e., $N_A! = N_B! = N_C! = N_D! = N_E! = N_i!$)

$$\mathrm{S} = \mathrm{k_B ln}\left[\frac{N!}{m(N_i!)n!}\right]$$

where m is the alloying number, and N_i is the number of atoms of each element in the system. N_i can be expressed in terms of N, n, and m: $N_i = \frac{N-n}{m}$. Substituting into the above equation gives:

$$\mathrm{S} = \mathrm{k_B ln}\left[\frac{N!}{m\left(\frac{N-n}{m}!\right)n!}\right]$$

and applying Stirling's approximation, which states that $\ln(x!) \approx x\ln(x)$:

$$\mathrm{S} = \mathrm{k_B}\left[\frac{N\ln(N)}{m\left(\frac{N-n}{m}\right)\ln\left(\frac{N-n}{m}\right)n\ln(n)}\right]$$

simplifies to

$$\mathrm{S} = \mathrm{k_B}\left[\frac{N\ln(N)}{(N-n)\ln\left(\frac{N-n}{m}\right)n\ln(n)}\right]$$

Re-written using the rule of logs:

$$\mathrm{S} = \mathrm{k_B}\left[N\ln(N) - (N-n)\ln\left(\frac{N-n}{m}\right) - n\ln(n)\right]$$

The configurational entropy is given by the differential with respect to n.

$$\Delta \mathrm{S} = \mathrm{k_B}\left[\ln\left(\frac{N-n}{m}\right) - \ln(n)\right]$$

which reduces to

$$\Delta \mathrm{S} = \mathrm{k_B}\left[\ln\left(\frac{N-n}{mn}\right)\right]$$

Alloy vacancy energetics

Assuming that n is small, i.e., $N - n \approx N$, and inversing the natural log

$$\Delta \mathrm{S} = -\mathrm{k_B} \ln\left(\frac{mn}{N}\right)$$

The Gibbs energy change with respect to n is therefore given by

$$\Delta \mathrm{G} = \Delta \mathrm{H} + \mathrm{k_B T} \ln\left(\frac{mn}{N}\right)$$

Rearranging for vacancy concentration, $\frac{n}{N}$,

$$\chi_v = \frac{n}{N} = \frac{1}{m} e^{\frac{-\Delta \mathrm{H}}{\mathrm{k_B T}}}$$