

Some Thermodynamic Constants for the Solution Processes of Atoms in Metallic Solvents

ShengNien Wang

Citation: *The Journal of Chemical Physics* **14**, 643 (1946); doi: 10.1063/1.1724080

View online: <http://dx.doi.org/10.1063/1.1724080>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/14/11?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Constants of the motion and diagonalization of the Hamiltonian for some scattering processes](#)
J. Math. Phys. **32**, 3361 (1991); 10.1063/1.529448

[The thermodynamic properties of electrolyte solutions: Some formal results](#)
J. Chem. Phys. **86**, 5110 (1987); 10.1063/1.452629

[Atomic Force Constants in Some First Row Compounds](#)
J. Chem. Phys. **57**, 4530 (1972); 10.1063/1.1678110

[Ion Solvent Interaction. VIII. Thermodynamic Properties of Ions in Methanol Solution](#)
J. Chem. Phys. **56**, 1606 (1972); 10.1063/1.1677412

[Grüneisen's Constant for Some Metals](#)
J. Chem. Phys. **23**, 1925 (1955); 10.1063/1.1740606



THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 14, NUMBER 11

NOVEMBER, 1946

Some Thermodynamic Constants for the Solution Processes of Atoms in Metallic Solvents

SHENG-NIEN WANG

2051 W. Grand Boulevard, Detroit 8, Michigan

(Received August 7, 1946)

By combining the gas-metal equilibrium data available in literature and the thermodynamic quantities of gaseous molecules and atoms from the method of statistical mechanics, thermodynamic constants for the solution processes of some atoms in some metallic solvents have been obtained.

I. INTRODUCTION

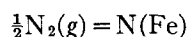
THE nature of solution in metallic solvents has been little understood. For instance, consider the case of carbon in iron. It would be of interest to know the nature of the interaction between the single carbon atom and its closest neighbors of iron atoms. It would be also of interest to inquire how much the presence of the carbon atom affects the electronic structure of the region around it. The solution of such problems must await the efforts of many investigators. In the present paper the author has endeavored to derive from the few available equilibrium studies between gas and metal a few thermodynamic constants of the solution processes by which an atom is transferred from the gaseous phase to the interior of metallic solvent.

II. METHOD OF EVALUATION

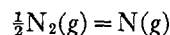
The equilibria considered here are those for which the quantitative relationship indicates that the solute exists inside the metallic solvent in atomic form.

The method used may be illustrated by the cases of the solution of nitrogen atom in iron and the solution of carbon atom in iron.

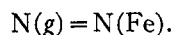
In the case of the nitrogen atom in iron, it is only necessary to combine the thermodynamic constants of the processes



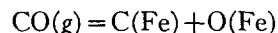
and



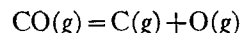
in order to obtain the thermodynamic constants of the process



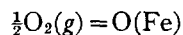
In the case of carbon in iron, a round-about way has to be used. To illustrate, the free energy change of the process



around 1600°C is known. The free energy change of the process



is obtained from the free energy values of the individual gases as obtained by the method of statistical mechanics as well as the energy change at absolute zero. In addition, free energy changes at 1600°C of both processes, namely,



and

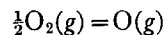


TABLE I. Equilibrium studies used in this paper.

Nature of equilibrium	Temperature range	Reference
$\frac{1}{2}\text{H}_2(\text{g})=\text{H}(\text{Fe})$	500°C–1650°C	a
$\frac{1}{2}\text{N}_2(\text{g})=\text{N}(\text{Fe})$	800°C–1540°C	a
$\frac{1}{2}\text{N}_2(\text{g})=\text{N}(\text{Fe})$	1600°C	b
$2\text{CO}(\text{g})=\text{CO}_2(\text{g})+\text{C}(\gamma\text{Fe})$	750°C–1150°C	c
$\text{H}_2\text{O}(\text{g})=\text{H}_2(\text{g})+\text{O}(\text{Fe})$	1600°C	d
$\text{H}_2\text{S}(\text{g})=\text{H}_2(\text{g})+\text{S}(\text{Fe})$	1600°C	e
$\text{CO}(\text{g})=\text{O}(\text{Fe})+\text{C}(\text{Fe})$	1540°C–1700°C	f
$\frac{1}{2}\text{H}_2(\text{g})=\text{H}(\text{Cu})$	530°C–1450°C	g
$\text{H}_2\text{O}(\text{g})=\text{H}_2(\text{g})+\text{O}(\text{Cu})$	1090°C–1350°C	h
$\text{SO}_2(\text{g})=2\text{O}(\text{Cu})+\text{S}(\text{Cu})$	1100°C–1300°C	i

^a A. Sieverts, G. Zaff, and H. Moritz, *Zeits. f. physik. Chemie* **A183** 19–37 (1938).

^b J. Chipman and D. Murphy, *Trans. A.I.M.E.* **116**, 179 (1935).

^c A. Bramley and H. D. Lord, *J. Chem. Soc. p.* 1641 (1932).

^d M. G. Fontana and J. Chipman, *Trans. Am. Soc. Metals* **24**, 329 (1936).

^e J. Chipman and Ta Li, *Trans. Am. Soc. Metals* **25**, 435 (1937).

^f S. Marshall and J. Chipman, *Trans. Am. Soc. Metals* **30**, 695 (1942).

^g P. Rontgen and F. Moller, *Metallwirtschaft* **13**, 81 (1934).

^h N. P. Allen and T. Hewitt, *J. Inst. Metals* **51**, 257 (1933).

ⁱ C. F. Floe and J. Chipman, *Trans. A.I.M.E.* **147**, 28 (1942).

are known. By combining all these values the free energy change of the process $\text{C}(\text{g})=\text{C}(\text{Fe})$ at 1600°C can be obtained.

III. LISTS OF EQUILIBRIA EXPERIMENTALLY STUDIED AND THERMODYNAMIC CONSTANTS THEORETICALLY EVALUATED USED IN THIS PAPER

The equilibrium studies used in this paper are listed in Table I.

The calculated values of free energies of the following gases are used in the calculations: C, H, O, S, CO, N₂, O₂, CO₂, H₂O, H₂S, and SO₂. Their origins are stated in the footnote.¹

The values of reaction energies at absolute zero of the reactions involved in the calculation are presented in Table II.

IV. RESULTS

The results of calculations will be presented in the form of tables in three categories, namely,

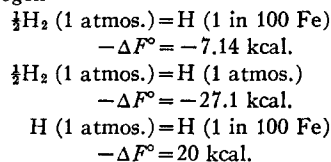
¹C: Calculated by the author based upon the energy values given by Goudsmit and Bacher in *Atomic Energy States* (1932). The values at 2000°K, 3000°K, and 4000°K check with the values given by A. R. Gordon (*J. Chem. Phys.* **5**, 352 (1937)) within 0.002 in terms of $(F^\circ - E_0^\circ)/T$. S: C. W. Montgomery and L. S. Kassel, *J. Chem. Phys.* **2**, 417 (1934). H and H₂: W. F. Giaque, *J. Am. Chem. Soc.* **52**, 4816 (1930). N and N₂: W. F. Giaque and J. C. Clayton, *J. Am. Chem. Soc.* **55**, 4875 (1933). O and O₂: H. L. Johnson and M. K. Walkers, *J. Am. Chem. Soc.* **55**, 187 (1933). CO: J. O. Clayton and W. F. Giaque, *J. Am. Chem. Soc.* **54**, 2622 (1932). CO₂: L. S. Kassel, *J. Am. Chem. Soc.* **56**, 1838 (1934). H₂O: A. R. Gordon, *J. Chem. Phys.* **2**, 65 (1934). H₂S: P. C. Cross, *J. Chem. Phys.* **3**, 168 (1935). SO₂: A. R. Gordon, *J. Chem. Phys.* **3**, 336 (1935). In cases, Murphy's formulae have been used (*J. Chem. Phys.* **5**, 637 (1937)).

molten iron as solvent, γ iron as solvent, and copper as solvent. For the first group only the free energy change at one single temperature (1600°C) will be given. For the latter two groups the free energy change can be obtained for a series of temperatures. Thus it is possible to calculate both the energy change and entropy change accompanying the solution process.

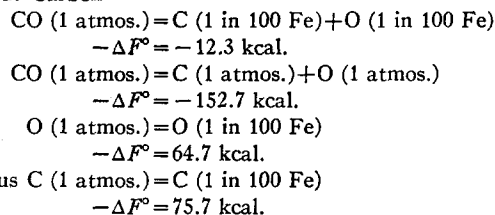
As usual, the state of fugacity equal to 1 atmos. is chosen as the standard state of the gaseous phase. For the solute the solute concentration of 1 atom of solute in 100 atoms of solvent, otherwise with the properties of a solute in an infinitely dilute solution, is chosen as the standard state.

A. Molten iron as solvent—At 1600°C

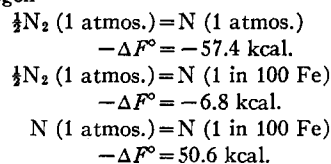
1. Hydrogen



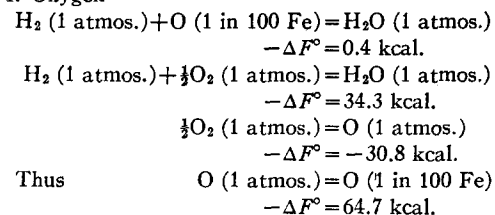
2. Carbon



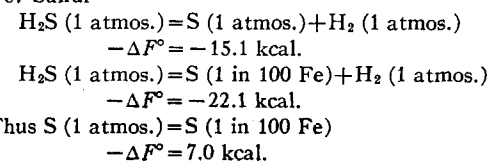
3. Nitrogen



4. Oxygen

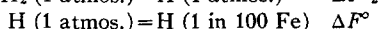
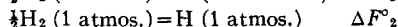
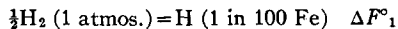


5. Sulfur

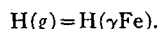


B. γ iron as solvent(1) Hydrogen— γ iron

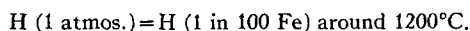
$T^\circ\text{C}$	$T^\circ\text{K}$	$-\Delta F^\circ_1/T$	$-\Delta F^\circ_2/T$	$-\Delta F^\circ/T$
1100	1373	-6.66	-26.44	19.78
1200	1473	-6.35	-23.79	17.44
1250	1523	-6.21	-22.59	16.38
1350	1623	-5.94	-20.42	14.48
1400	1673	-5.86	-19.42	13.56



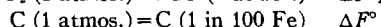
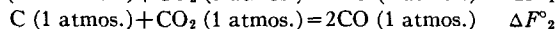
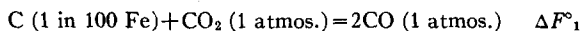
$-\Delta E^\circ$ is equal to 44 kcal. for the reaction



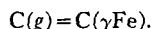
$-\Delta S^\circ$ is equal to 14.4 cal. per mole per degree for the reaction

(2) Carbon— γ iron

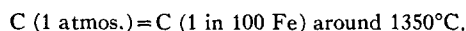
$T^\circ\text{C}$	$T^\circ\text{K}$	$-\Delta F^\circ_1/T$	$-\Delta F^\circ_2/T$	$-\Delta F^\circ/T$
827	1100*	2.66	82.48	79.82
877	1150*	3.83	79.06	75.23
927	1200	4.97	75.92	70.96
977	1250	5.99	73.03	67.05
1027	1300	6.82	70.36	63.54
1077	1350	7.59	67.84	60.26



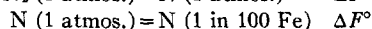
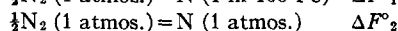
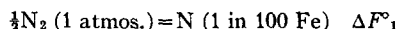
$-\Delta E^\circ$ is equal to 113 kcal. for the reaction



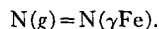
$-\Delta S^\circ$ is equal to 25.2 cal. per mole per degree for the reaction

(3) Nitrogen— γ iron

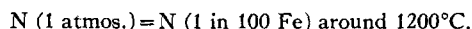
$T^\circ\text{C}$	$T^\circ\text{K}$	$-\Delta F^\circ_1/T$	$-\Delta F^\circ_2/T$	$-\Delta F^\circ/T$
1400	1673	-5.30	-36.21	30.91
1390	1663	-4.93	-36.52	31.59
1380	1653	-4.89	-36.84	31.95
1310	1583	-4.86	-39.16	34.30
1300	1573	-4.77	-39.51	34.74
1200	1473	-4.66	-43.27	38.61



$-\Delta E^\circ$ is equal to 90 kcal. for the reaction



$-\Delta S^\circ$ is equal to 24.5 cal. per mole per degree for the reaction



* For the temperatures 1100°K and 1150°K, γ iron phase is stable only when the carbon concentrations are above certain values.

TABLE II. Energies of reactions at absolute zero.*

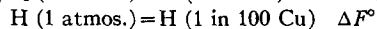
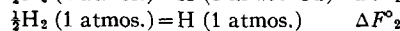
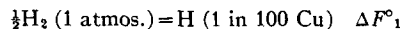
Reaction	Increase in energy content at absolute zero in kcal. ΔE°
$\text{H}_2(\text{g}) = 2\text{H}(\text{g})$	103.2
$\text{O}_2(\text{g}) = 2\text{O}(\text{g})$	117.2
$\text{N}_2(\text{g}) = 2\text{N}(\text{g})$	170.2
$\text{CO}(\text{g}) = \text{C}(\text{g}) + \text{O}(\text{g})$	210.8
$\text{H}_2\text{S}(\text{g}) = \text{H}_2(\text{g}) + \frac{1}{2}\text{S}_2(\text{g})$	19.6
$\frac{1}{2}\text{S}_2(\text{g}) = \text{S}(\text{g})$	42
$\text{H}_2\text{S}(\text{g}) = \text{H}_2(\text{g}) + \text{S}(\text{g})$	61.6
$\text{SO}_2(\text{g}) = \frac{1}{2}\text{S}_2(\text{g}) + \text{O}_2(\text{g})$	85.9
$\text{H}_2\text{O}(\text{g}) = \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$	57.8
$2\text{CO}_2(\text{g}) = 2\text{CO}(\text{g}) + \text{O}_2(\text{g})$	133.5

* The references to these values in Table II are the same as those in the previous footnote (reference 1) except that $\frac{1}{2}\text{S}_2(\text{g}) = \text{S}(\text{g})$ and $\text{N}_2(\text{g}) = 2\text{N}(\text{g})$ are from *Molecular Spectra and Molecular Structure* by Herzberg and that $\text{CO}(\text{g}) = \text{C}(\text{g}) + \text{O}(\text{g})$ is also due to Herzberg (*J. Chem. Phys.* 10, 306 (1942)).

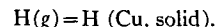
C. Copper as solvent

(1) Hydrogen—solid copper

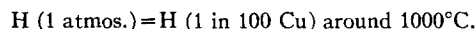
$T^\circ\text{C}$	$T^\circ\text{K}$	$-\Delta F^\circ_1/T$	$-\Delta F^\circ_2/T$	$-\Delta F^\circ/T$
843	1116	-11.04	-35.40	24.36
995	1268	- 9.72	-29.67	19.95
1074	1347	- 9.02	-27.19	18.18



$-\Delta E^\circ$ is equal to 37.5 kcal. for the reaction



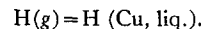
$-\Delta S^\circ$ is equal to 11.5 cal. per mole per degree for the reaction



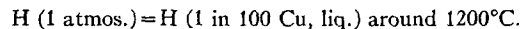
(2) Hydrogen—liquid copper

$T^\circ\text{C}$	$T^\circ\text{K}$	$-\Delta F^\circ_1/T$	$-\Delta F^\circ_2/T$	$-\Delta F^\circ/T$
1106	1379	-6.86	-26.27	19.42
1128	1401	-6.72	-25.66	18.94
1180	1453	-6.43	-24.29	17.86
1312	1585	-5.82	-21.21	15.40
1450	1723	-5.11	-18.49	13.38

$-\Delta E^\circ$ is equal to 39 kcal. for the reaction

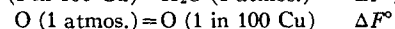
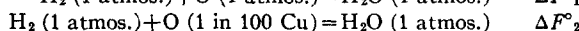
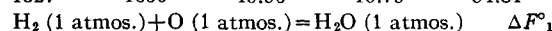


$-\Delta S^\circ$ is equal to 9 cal. per mole per degree for the reaction

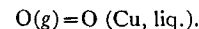


(3) Oxygen—copper (liq.)

$T^\circ\text{C}$	$T^\circ\text{K}$	$-\Delta F^\circ_1/T$	$-\Delta F^\circ_2/T$	$-\Delta F^\circ/T$
1127	1400	56.29	13.00	43.29
1177	1450	53.33	12.39	40.94
1227	1500	50.57	11.80	38.77
1277	1550	47.98	11.27	36.71
1327	1600	45.56	10.75	34.81



$-\Delta E^\circ$ is equal to 92 kcal. for the reaction



$-\Delta S^\circ$ is equal to 24.5 cal. per mole per degree for the reaction

O (1 atmos.) = O (1 in 100 Cu) around 1200°C.

(4) Sulfur—copper (liq.)

$T^\circ\text{C}$	$T^\circ\text{K}$	$-\Delta F^\circ_1/T$	$-\Delta F^\circ_2/T$	$2. -\Delta F^\circ_3/T$	$-\Delta F^\circ/T$
1127	1400	-2.23	-114.94	86.58	26.13
1177	1450	-1.47	-108.78	81.88	25.43
1227	1500	-0.77	-103.02	77.54	24.72
1277	1550	-0.11	-97.64	73.42	24.11
1327	1600	+0.51	-92.59	69.60	23.51

SO_2 (1 atmos.) = S (1 in 100 Cu) + 2O (1 in 100 Cu) ΔF°_1
 SO_2 (1 atmos.) = S (1 atmos.) + 2O (1 atmos.) ΔF°_2
 O (1 atmos.) = O (1 in 100 Cu) ΔF°_3
 S (1 atmos.) = S (1 in 100 Cu) ΔF°

$-\Delta E^\circ$ is equal to 26 kcal. for the reaction

$\text{S(g)} = \text{S(Cu, liq.)}$.

$-\Delta S^\circ$ is equal to 5.5 cal. per mole per degree for the reaction

S (1 atmos.) = S (1 in 100 Cu) around 1200°C.

V. DISCUSSION

In view of the present inadequacy of our knowledge about the metallic state the discussion offered here will be brief and qualitative.

The case of hydrogen atom as solute is different from those of other atoms, inasmuch as the hydrogen atom (or rather the proton) is essentially free to roam all over the free volume of the metal while the other atoms as solute are restricted by surrounding solvent atoms. Therefore in a general treatment of solutions of hydrogen in metals where the solvent lattice is preserved (such as hydrogen in copper, iron, nickel, cobalt, etc.), Fowler and Smithells² used a picture of protons as a gas enclosed inside the free volume of the metallic solvent. The solutions of carbon and nitrogen in metals perhaps could be pictured as the random distribution of the atoms (in dilute solution, at least) among the interstices (slightly enlarged), with the atoms behaving as three-dimensional oscillators inside the interstices. It is to be noted that the entropy changes attending the solution processes of carbon and nitrogen atoms in γ -iron are nearly equal.

The energy changes attending the solution processes are summarized below:

Process	$-\Delta E^\circ$	Process	$-\Delta E^\circ$
$\text{H(g)} = \text{H}(\gamma\text{Fe})$	44 kcal.	$\text{H(g)} = \text{H(Cu, liq.)}$	39 kcal.
$\text{C(g)} = \text{C}(\gamma\text{Fe})$	113 kcal.	$\text{O(g)} = \text{O(Cu, liq.)}$	92 kcal.
$\text{N(g)} = \text{N}(\gamma\text{Fe})$	90 kcal.	$\text{S(g)} = \text{S(Cu, liq.)}$	26 kcal.

² R. H. Fowler and C. J. Smithells, Proc. Roy. Soc. **160**, 37 (1937).

Consider the cases of carbon and nitrogen in austenite. The metallic radius of the iron atom in γ iron (f. c. c.) is 1.26Å.³ The carbon atoms, and the nitrogen atoms presumably, are distributed in the octahedral interstices.⁴ A sphere of diameter 1.04Å can be inscribed in the octahedral interstices of pure γ -iron. Thus even carbon and nitrogen with single covalent radii of 0.77 and 0.70Å,⁵ respectively, have to push out the surrounding iron atoms to certain extent in order to accommodate themselves. A crude estimate of the lattice expansion due to the addition of carbon atom is as follows: G. Hagg⁶ mentioned that the axial length of austenite containing 0.9 percent carbon is 3.58Å while that of pure γ iron is 3.56Å. The expression $(3.58)^3 - (3.56)^3$ thus denotes the average increase in size of the unit cell as the result of the addition of carbon for the amount of 0.9 weight percent. The composition of 0.9 percent carbon corresponds to an iron and carbon number ratio of 24 to 1. If all octahedral interstices were filled with carbon atoms and the contribution towards volume increase for each carbon atom were still equal to the amount when the solution is dilute, the size of a unit cell of such a hypothetical crystal, of equal numbers of iron and carbon atoms and of a structure like NaCl, would be $[(3.58)^3 - (3.56)^3] \times 24 + (3.56)^3$, i.e., 65.7Å³. The axial length for such a unit cell is $(65.7)^{1/3}$, i.e., 4.0Å. It would be equal to two times the radius of the iron atom plus two times the radius of the carbon atom, the value of the radii being those in the state of chemical combination between carbon and iron as in the dilute austenite. Using the covalent radius of 0.77Å for carbon and the metallic radius of 1.26Å for iron, we get the value of 4.06Å. The agreement is good, indicating that the assignment of covalent radius to carbon and metallic radius to iron is a rather fair approximation.

The energy decrease accompanying the solution of a carbon atom into the γ iron lattice, i.e., 113 kcal., is the resultant of the energy increase in the expansion of the lattice and the energy decrease in the filling of the cavity with carbon

³ L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, New York, 1940), p. 390.

⁴ N. J. Petch, J. Iron and Steel Inst. **145**, No. I, 111 (1942).

⁵ L. Pauling, reference 3, p. 154.

⁶ G. Hagg, J. Iron and Steel Inst. **130**, No. II, 439 (1934).

atom. The same type of consideration should also be true of the solution of nitrogen in γ iron lattice.

The cases of oxygen and sulfur in copper are similar. Although we are dealing with the liquid phase of copper, we may still consider the arrangement of copper atoms as close packed inasmuch as only the short range order is important. According to Fowler and Guggenheim,⁷ "a recent experimental study by Lark-Horowitz of the scattering of x-rays by liquids has shown that the average value of the number of closest neighbors for normal liquids is close to eleven."

Consider the copper atoms in the close packed structure as spheres having a radius of 1.28\AA .³ The radius of an oxygen atom in the metal should be somewhere between the single covalent radius of 0.66\AA ⁵ and the bivalent ionic radius of 1.40\AA .⁸ The radius of a sulfur atom similarly is somewhere between the covalent radius of 1.04\AA ⁵ and the bivalent ionic radius of 1.84\AA .⁸ Because of the strong electronegative character of oxygen and sulfur, unlike carbon, the covalent radius cannot be taken as an approximation. It can only be said that the work spent on the creating of the cavity for the oxygen atom and also for the sulfur atom to be accommodated would be considerable.

⁷ R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, New York, 1939), p. 345.

⁸ L. Pauling, reference 3, p. 330.

Although our results in regard to the processes with molten iron as solvent are restricted to a single temperature, namely 1600°C , and to one kind of thermodynamic constant, namely free energy change, a short remark may be made about the solutions of carbon and nitrogen in molten iron.

As noted before, the entropy changes attending the solution processes of carbon and nitrogen atoms in γ iron are nearly equal. It is probable that the entropy changes of the similar processes in molten iron are also nearly equal. The difference in free energy change would then be equal to the difference in energy change. The difference between the free energies of solution of carbon and nitrogen in molten iron is nearly equal to the difference between the energies of solution of carbon and nitrogen atoms in γ iron as is shown in the summary below:

Process	$-\Delta F^\circ$ in kcal.	Process	$-\Delta E^\circ$ in kcal.
C(1 atm.) = C(1 in 100 Fe, liq.)	75.7	C(g) = C(γ Fe)	113
N(1 atm.) = N(1 in 100 Fe, liq.)	50.6	N(g) = N(γ Fe)	90
Difference	25.1		23

Thus the supposition of the equivalence in entropy change is tantamount to saying that the difference in the energies of solution of carbon and nitrogen atoms in iron would be only minorly affected by the phase change and the temperature difference of few hundred degrees.