

Molar Heat Capacities of Metals Depend on Crystal Structures Thermal Properties of the Elements

Johann Marinsek marinsekaon.at

0,128 Joule is needed to heat 1 g of gold (Au) by 1°K. 0,128 J/g K is by definition the specific heat of Au. The atomic mass number of Au is $A = 197$. Below I show that the molar heat of Au is 0,128 times 197: $0,128 \times 197 = 25,22$ J/mol K and not (according to current theory) 0,128 times 196,96654 = 25,21. The so-called atomic weight of Au, namely 196,96654 has nothing to do with the amount of matter or *quantitas materiae* but is a dynamical property. An accelerated atom of Au experiences a drag force by an electromagnetic medium. This force is proportional to ma , where a is acceleration and m the erroneously so-called inertial mass. The inertial mass is slightly smaller than A and it is measured not for the atom but for the ion of the atom. (By convention the inertial mass of carbon is 12.) Therefore the inertial mass is irrelevant for the concept of a mole: a mole of a substance is the quantity of matter in grams that is numerically equal to the atomic (or molecular) matter units. In stoichiometric equations like

$2H_2 + O_2 \Rightarrow 2 H_2O$ two moles of hydrogen react with one mole of oxygen, giving two moles of water. Obviously these quantitative relations have nothing to do with the inertial masses of hydrogen or oxygen but with *quantitas materiae*. According to Prout all elements are made up of hydrogen. The atomic mass number A is the number of hydrogen atoms that constitute an element, so Au is made up of 197 hydrogens. A mole of Au is 197 grams of Au. Silver is a 51,84:48,16 mixture of ^{107}Ag and ^{109}Ag , a mole silver is therefore 107,96 grams and not the reported 107,868, which is the inert mass. The correct molar heat is 25,05 and not the erroneously with the irrelevant inert mass calculated 25,3 J/mol K.

Molar heat capacity for ideal gases

One mole of a gas contains $6,022 \cdot 10^{23}$ molecules: $N_A = 6,022 \cdot 10^{23}$ /mol ...denotes Avogadro's number. The ideal gas law states:

$$PV = n RT = N_A kT$$

Where n = number of moles, k = Boltzmann constant = $1,381 \cdot 10^{-23}$ J/K and R = universal gas constant = 8,3145 J/mol K.

According to the kinetic theory of ideal gases the average translational kinetic energy of any kind of atom or molecule per mole is given by $E_{kin} = 3R/2$. This value is in good agreement with empirical heat capacities per mole for monatomic gases, see the table below.

Specific heat capacities of gases at 25° C, 1 bar [Paus]

	c_p J/kgK	C_p J/mol K	C_v J/mol K	$C_p - C_v$	
He	5233	20,93	12,61	8,32	$C_p \approx C_v + R$ $C_v \approx 3R/2 = 12,47$ J/mol K
Ne	103	20,79	12,48	8,31	
Ar	523	20,91	12,48	8,43	
Kr	248	20,91	12,37	8,54	
Xe	160	20,98	12,64	8,34	
H ₂	14300	28,83	20,45	8,38	$C_p \approx C_v + R$ $C_v \approx 5R/2 = 20,79$ J/mol K
Cl ₂	473	<u>33,56</u>	<u>24,84</u>	8,72	
N ₂	1041	29,15	20,81	8,34	
O ₂	917	29,31	21,12	8,19	

Comment: Paus calculated for the molar heat capacity: $C_p \text{ J/mol K} = c_p \text{ J/kgK}$ times inertial mass of the element or molecule. For example for Kr: $248 \times 83,8 = 20,78 \text{ J/mol K}$. This is a flaw, see above. In order to calculate the molar heat capacity the amount of matter must be used. Kr is mixture of isotopes, for example $^{84}\text{Kr} = 57\%$, $^{86}\text{Kr} = 17,3\%$, $^{83}\text{Kr} = 11,5\%$,... One mole Kr is 84,31. $248 \times 84,31 = 20,91 \text{ J/mol K}$! For the other elements in the table the difference is smaller.

The relationship for ideal gases: $C_p = C_v + R$ is empirically confirmed for both elements and molecules.

The illustrations show the meaning of the formula. If we supply heat to a gas that can expand at a constant pressure then a part of the heat goes to doing external work, namely to elevate the weight. The other part of the heat goes to raising the temperature of the enclosed gas. If we keep the volume of the gas constant then the entire amount of heat that we supply goes towards raising the temperature of the gas! This is the reason that the molar heat capacity is greater if the gas was held at a constant pressure than if the gas is forced to remain at a constant volume. Therefore we have a molar heat capacity at constant pressure: C_p and a molar heat capacity at constant volume C_v and $C_p > C_v$.

For monoatomic gases the molar heat capacities are nearly the same, but there are significant different values for diatomic gases.

How can we interpret this behaviour? Obviously heat is not only stored in the translational and rotational motion but is also stored as potential energy in the elastic bonds of the molecule. For diatomic gases this potential energy is comparatively small, but for metals it is the main part of energy. (See below.)

Molar heat capacities of metals depend on crystal structure

According to the prevailing quantum theory metallic bonding is an interplay of the free valence electrons that constitute the so-called electron cloud and the ion cores of the lattice atoms. The electrons allegedly drift in a random manner through the lattice of ion cores. The bonding model explains metals as a lattice of ion cores held together by a gas of free electrons! This is an untenable explanation. The electron gas cannot hold together the ion cores that are repelling each other!

Here I propose an atomic model according to William Prout (1815): each chemical element is made out of hydrogen atoms. The so-called mass numbers A represent the number of the constituting hydrogen atoms. Bonding is due to magnetic coupling because each hydrogen atom is a magnet. Conjecture: Hydrogen itself is composed of 4 elementary ring magnets that are charged $+ - + -$.

Molecules are atoms conjoined in some way. Bonding in molecules is also due to magnetic coupling. There is neither ionic nor covalent bonding (electron sharing) because there are no extranuclear electrons. Bonding agents are hydrogen atoms.

There are 3 varieties of H-bonds:

single hydrogen,

2 hydrogen atoms in series — —

or 2 hydrogen bonds parallel ||.

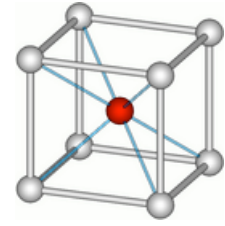
Molar heat capacity depends on the crystal structure of the element or molecule and on hydrogen bonding.

The known crystal structures and heat capacities indicate the existing hydrogen bonding.

Case studies for body centred cubic (bcc), face centred cubic (fcc) and hexagonal close-packed (hcp) crystal structures.

In the first row the supposed hydrogen bonding is mentioned.

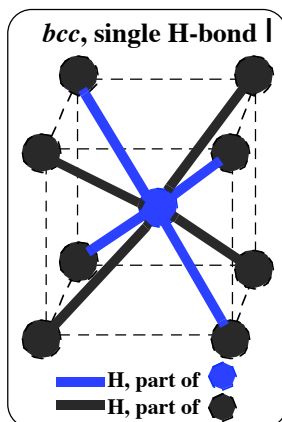
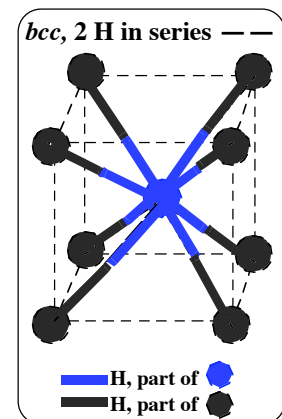
Because electromagnetic properties are due to crystal structure and bonding the sign of the Hall effect coefficient $\pm R_H$ and the nature of magnetism (where f = ferromagnetic, p = paramagnetic, d = diamagnetic) are specified. The next two rows show electrical conductivity and superconductivity properties. Molar volume and rigidity modulus (= shear modulus) indicate the nature of bonding. The graph from wikipedia shows the conventional bcc unit cell.



Bcc: bonding:	Li: single H, 2 H's in series					
Element	Li	Na	K	Rb	Cs	Ba
c_m : molar heat [J/mol K]	24,8	28,3	29,5	31	31,9	28
Sign of Hall effect constant R_H	—	—	—	—	—	?
Para-, ferro-, diamagnetic: f, p, d	P	P	P	P	P	P
El. conductivity $10^6 / \text{cm}\Omega$	11	2	14	8	5	33
Superconductivity	Li	—	—	—	Cs	Ba
A: lattice spacing [10^{-11} m]	35	43	53	56	61	50
Molar volume [cm^3]	13	23,8	45,9	55,8	70,9	38,2
Rigidity modulus [GPa]	4,2	3,3	1,3	—	—	4,9

Comment: minor and not linear dependence of c_m on matter number A. c_m is for Na, K, Rb, Cs, and Ba in the same range. c_m is a lattice parameter; increase of lattice spacing coincides with increase of molar heat capacity and decrease of rigidity. The lattice has a bcc structure.

For a bcc structure there are 8 nearest neighbours per atom (the coordination number is 8). Here the bonds are assumed to consist of complete hydrogen atoms. Because of the relatively large lattice spacing these 8 material bonds are thought of as 2 hydrogen atoms in series. Every atom consists of a core and 8 magnetically coupled hydrogen atoms that function as bonds (see the illustration). Na for example has a core that consists of $23 - 8 = 15$ hydrogen atoms. See the article *All Elements Consist of Hydrogen*.



Li is a special case: it has the smallest lattice spacing and therefore also the smallest molar heat capacity. The 8 bonds are thought of as single hydrogen atoms. The core has $7 - 4 = 3$ Hydrogen atoms. 4 hydrogen bonds are from the Li atom, the other necessary 4 hydrogen bonds are from the 8 nearest neighbours (bond sharing).

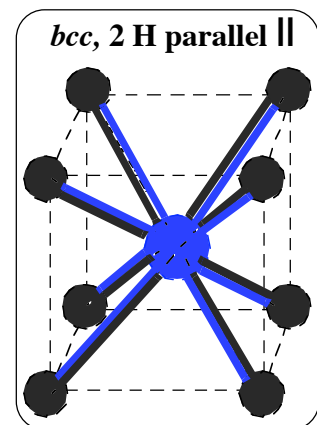
Note that all alkali metals are paramagnetic and have negative sign for the Hall constant.

Lattice spacing (or molar volume) and rigidity modulus (= shear modulus) are in the same range!

Element	Bcc metals			2 H's parallel				Single H ?			
	⁵² Cr	mix Mo	mix W	⁵⁶ Fe	⁹³ Nb	⁵¹ V	¹⁸¹ Ta				
c_m	23,3	24	23,9	25,1	23,2	24,9	25,3				
R_H	+	+	+	+	+	+	+				
f, p, d	P	D	P	F	P	P	P				
$10^6/m\Omega$	7.7	19	19	10	7	5	7.6				
Superconductivity	—	Mo	W	Fe	Nb	V	Ta				
A [⁻¹¹ m]	29	31	32	29	33	30	33				
/Gpa	115	121	160	82	38	47	69				

Comment: minor and not linear dependence of c_m on matter number A. c_m is for Cr, Fe, W, Mo, Nb, Ta and V in the same range. c_m is a lattice parameter; increase of lattice spacing coincides in most cases with increase of molar heat capacity and decrease of rigidity, for example for W and Mo: nearly the same lattice spacing, molar heat capacity and rigidity! Fe is a bit irregular.

Because of the relatively small lattice spacing in the range of 300 pm the bonding seems to be a 2-hydrogen parallel bond. Note that the mentioned metals are paramagnetic respective ferromagnetic (Fe) and have positive sign for the Hall constant. An exception is Mo that is diamagnetic. Lattice spacing (or molar volumes) is in the same range.

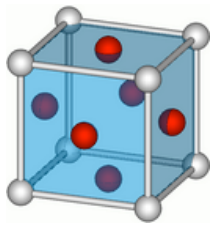


Fcc structure

	2 H's parallel		2 H's in series — —						2 H's in series	
	Ir	Rh	Al	Cu	Ag	Au	Pd	Pb	Ca	Sr
c_m	25	24,9	24,3	24,5	25,3	25,2	26	26,7	25,9	26,3
R_H	+	—	—	—	—	—	—	+	—	—
f,p, d	P	P	P	D	D	D	P	D	P	P
$10^3 -/cm\Omega$	197	211	377	596	630	452	95	48	298	76
Supercond.	Ir	Rh	Al	—	—	—	—	Pb	Ca	Sr
$a^{-11}m$	38	38	40	36	41	41	39	49	56	61
Molar vol	8,52	8,28	10	7,11	10,3	10,2	8,56	18,3	26,2	33,9
Gpa	210	150	26	48	30	27	44	46	7,4	6,1

Comment:

See the article Electricity where the details of the fcc structure are explained. The bonds in this model are physical bonds, they consist of complete hydrogen atoms. The bonds consist of 2 H's parallel || or in series — —. The little cube shows the conventional fcc unit cell.



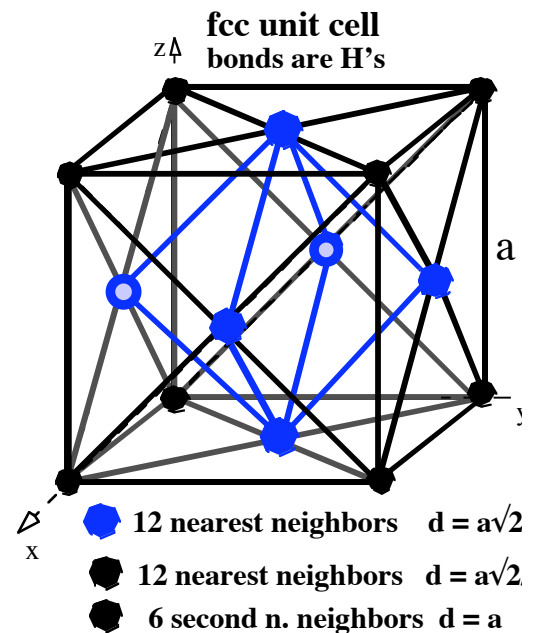
The co-ordination number for a fcc crystal structure is 12, therefore there are 12 hydrogen bonds possible. Example Al: Core: $27 - 12 = 15$.

Exceptions are Ir with its great rigidity and Ca, Sr with its small rigidities. Note that Ag and Au have nearly the same value for molar heat capacity, 25,3; 25,2, respectively. Note also that Ag and Au have nearly the same molar volume: 10,27 vs. 10,21/cm³. Some other parameters for Ag and

(Au): Young's modulus 83, (78) Gpa; mineral hardness: 2,5, (2,5); reflectivity: 97, (95) %; melting 1235, (1337). All thermodynamic properties of Ag and Au have nearly the same value!

Imagine the lattice of Ag or Au as an elastic 3D-mattress. Both lattice spacing and lattice structure of Ag and Au are the same. The sole difference between Ag- and Au mattress concerns the lattice points. If 12 hydrogen atoms serve as bonds to the 12 nearest neighbours, the core in a lattice point of silver is: $107 - 12 = 95$ for ¹⁰⁷Ag or $109 - 12 = 97$ for ¹⁰⁹Ag.

For ¹⁹⁷Au: $197 - 12 = 185$. The atomic cores in the lattice points and the hydrogen linkages are connected by magnetic coupling. Obviously the elasticity of this coupling depends on the configuration of the cores and their quantity of hydrogen constituents.



Hcp-structure

	Os	Ru	Mg	Sc	Ti	Zn	Zr	Cd	Hf	Tc	Co	Be
c_m	24,7	24,1	24,8	25,5	25	25,7	25,4	26,2	25	24,5	24,8	15,8
R_H	?	+	—	—	?	+	+	+	+	+	—	?
F, P, D	P	P	P	P	P	D	P	D	D	P	F	D
$10^6/m\Omega$	11	14	23	1,8	2,3	17	2,4	14	3,1	7	17	31
<i>Supercond.</i>	<i>Os</i>	<i>Ru</i>	—	<i>Sc</i>	<i>Ti</i>	<i>Zn</i>	<i>Zr</i>	<i>Cd</i>	<i>Hf</i>	<i>Tc</i>	—	<i>Be</i>
a	27	27	32	33	30	27	32	30	32	27	25	22
/c	/43	/43	/52	/53	/47	/50	/51	/56	/50	/44	/41	/36
[/ cm ³]	8,4	8,2	14	15	10,6	9,2	14	13	13,4	8,6	6,7	4,9
Gpa	222	173	17	29	44	43	33	19	30	—	75	132

Comment: concerning lattice spacing or molar volume, rigidity and molar heat capacities the fcc-structured metals are in the same range. Excepted is Be. Be has the smallest molar volume $V = a^2c$ and therefore a great stiffness. Its molar heat capacity is significant lower.