



Thermodynamics of circular CrO₃ clusters sensitivity to various gases: A DFT study

Mudar Ahmed Abdulsattar, Mahdi M. Mutter, Attarid M. Oufi, Ausama I. Khudiar*

Ministry of Science and Technology, Baghdad, Iraq.

Abstract

The interaction of circular chromium trioxide clusters with various gases is discussed using density functional theory. Circular (CrO₃)_n clusters with n=1 to 6 are investigated. The interacting gases include CO, H₂, NH₃, CH₄, and O₂. All the interacting gases pick oxygen atoms from CrO₃ clusters (except O₂) leaving an oxygen-deficient cluster while O₂ in ambient air re-oxidize these clusters. The CrO₃ oxygen-deficient cluster has a lower energy gap that promotes the sensitivity of these clusters to the interacting gases. Thermodynamics of the interaction that includes the evaluation of Gibbs free energy, enthalpy, and reaction entropy is discussed. The variation of reaction temperature shows the temperature ranges in which reactions take place using Gibbs energy values. Some of the gas reactions are exothermic or endothermic depending on the enthalpy's values. Natural bond orbitals (NBO) analysis shows the charges on each atom in the CrO₃ cluster and gases. These charges explain the reaction electrostatics between the clusters and gases. The gas relative sensitivity to these gases can be calculated using the change in the energy gap and reaction rate.

Keywords: CrO₃; Density Functional Theory; Energy gap; Gibbs free energy; Enthalpy.

Full length article *Corresponding Author, e-mail: mudarahmed3@yahoo.com

1. Introduction

Chromium trioxide is an important material that is used as a catalyst and a gas sensor [1,2]. Having the highest oxidization state of Cr results in the use as an oxidizer [3,4]. It is one of several oxides of chromium that include CrO, Cr₂O₃, CrO₂, ...etc with varying oxygen content [5]. CrO₃ represents the fully oxidized and highest oxygen content of its oxides. Some of these oxides are magnetic so that they can be applied in a tape recording, such as CrO₂ [5]. The energy gap of bulk CrO₃ is 3.14 eV [1,6]. Depending on the structure, X-ray diffraction, IR and Raman spectroscopy can be used to discriminate these oxides from each other. Experimental Raman spectra of CrO₃ are reported in reference [7] with the LO mode at 970 cm⁻¹.

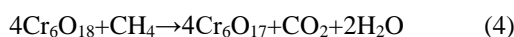
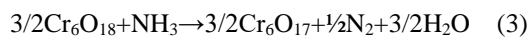
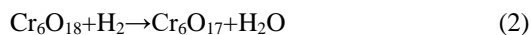
Because CrO₃ is fully oxidized, most gases react with this material by picking oxygen atoms from this compound [2]. Examples of these gases include CO, H₂, NH₃, and CH₄. The remaining oxygen-deficient clusters can be re-oxidized by oxygen gas molecules. The reactivity and thermodynamics of CrO₃ are rarely discussed [8,9]. The reaction of CrO₃ with the above gases depends on the temperature and number of oxygen atoms required to burn

the gas. The present electronic and magnetic applications of CrO₃ is an important motivation for further research of different properties of CrO₃ [10,11].

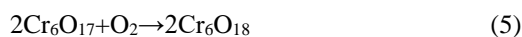
This work aims to use density functional theory (DFT) to calculate the reactions of several gases with Chromium trioxide small clusters including CO, H₂, NH₃, and CH₄ common gases that are normally most of the detected gases in gas sensors [12].

2. Materials and methods

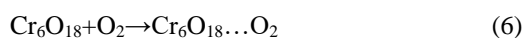
The interaction of CrO₃ clusters with the incoming gas molecules includes the removal of an oxygen atom or more from the CrO₃ cluster that oxidizes the gas molecule. Small cyclic CrO₃ clusters were suggested in reference [6]. The length of the largest considered cluster (Cr₆O₁₈ molecule) is 0.9 nm. These clusters are used to investigate CrO₃ clusters reactions in the present work and are shown in Fig. 1. The reactions of considered gases CO, H₂, NH₃, and CH₄ with the largest cluster Cr₆O₁₈ are given by:



The CrO₃ clusters that lost one oxygen atom are shown in Fig. 2. When the gas flow stops, and the normal air flows over CrO₃ clusters, the following reaction proceeds:



In contrast to chemisorption reactions (Eq. (1-4)), the interaction of oxygen with the fully oxidized CrO₃ clusters is called physisorption as in the following equation:



The three points (...) in the above equation refers to van der Waals forces connection.

In a gas sensor, several factors affect its sensitivity to a particular gas. The sensitivity (R_a/R_g) is given by the ratio of the ambient gas resistance (R_a) to resistance in the presence of the detected gas (R_g) in the case of reducing gases or its reciprocal (R_g/R_a) in the case of oxidizing gases [13]. The energy gap of materials is related to the conductivity by the following equations [14]:

$$\sigma = \sigma_0 \exp\left(\frac{-E_g}{2k_B T}\right) \quad (7)$$

$$\sigma_0 = C T^{\frac{3}{2}} q_e (\mu_e + \mu_h), \quad (8)$$

where σ , σ_0 , and k_B are the electrical conductivity, pre-exponential factor, and Boltzmann's constant, respectively. Also, in the pre-exponential factor, C is some constant, q_e is electron's charge, μ_e and μ_h are electron's and hole's mobility, respectively.

The response and recovery time can be evaluated in terms of the reaction rate of the monitored gas with sensitive oxide. The reaction rate is given by [15]:

$$k(T) = \frac{k_B T}{hc} \exp\left(\frac{-\Delta G}{k_B T}\right). \quad (9)$$

k_B is Boltzmann constant, h is Planck's constant, c is the concentration, ΔG is the change in Gibbs free energy of reaction. From Eqs. (7-9) we can see that most of the quantities are constants and can be omitted in calculating the

relative temperature-dependent sensitivity so that the sensitivity (in the reduction case) for a given temperature can be proportional to:

$$\text{Sensitivity}(T) = \frac{R_a}{R_g} \sim \exp(E_{ga} - E_{gg}) k(T) \quad (10)$$

E_{ga} is the energy gap in the ambient air and E_{gg} is the energy gap in the presence of the detected gas.

In addition to the energy gap and thermodynamic quantities described above, there are also other factors that influence the sensitivity of the oxide clusters to gases. From these factors are:

- 1- The gas concentration is probably the most required quantity that is determined frequently in gas sensors operation [16,17].
- 2- The kind of reaction that determines how many oxygen atoms are picked from CrO₃ clusters for every single molecule of the interacting gas. All the Eqs. (1-5) are normalized to a single incident gas molecule. However, CH₄ picks four oxygen atoms while the H₂ molecule picks only one atom from the oxide cluster.
- 3- The stripping of oxygen atoms is not limited to one oxygen atom [18]. Higher concentrations can strip several oxygen atoms from each surface cluster. If all oxygen atoms are stripped from a cluster the remaining Cr metal cluster is of very low resistivity.
- 4- Some molecules can diffuse more deeply than other molecules such as H₂ [19]. When these molecules reach inside clusters, the probability of forming surface Cr clusters (with no oxygen atoms) are more probable.
- 5- The grain size of the particles is of great importance so that gas molecules can reach most of the surface atoms for small or nano-thin films [20].

All calculations are performed using B3LYP hybrid density functional theory and 6-311G** basis states. Gaussian 09 program is used throughout the calculations [21].

3. Results and Discussions

Fig. 3 shows the variation of the energy gap of (CrO₃)_n clusters. The energy gap of oxygen-deficient clusters is also shown. Different values of bulk CrO₃ are measured experimentally that have a range of values 2.25, 3.14, and 4.32 eV [1,6,22]. As we can see from Fig. 3 that the lowest value of 2.25 eV might have been generated because of oxygen deficiency. In the present work, we recommend the midst value of 3.14 eV. The fully oxidized clusters energy gap seems to converge towards this value as expected from the quantum confinement theory. The difference between oxidized and vacancy clusters is in the range of less than 1 to 1.5 eV.

Fig. 4 shows the Gibbs free energy and enthalpy of reaction of H₂ molecule with the largest CrO₃ investigated cluster of Eq. 2 as a function of temperature. We can see from this figure that this reaction is exergonic (spontaneous) in the temperature range from ambient temperature to the end of the investigated range because of the negative values of Gibbs free energy of the reaction. The Gibbs free energy of the reaction is given by:

$$\Delta G = \Delta H - \Delta S T \quad (11)$$

where ΔH and ΔS are the change in the enthalpy and entropy of reaction, respectively, and T is the temperature. Fig. 5 shows the positive values of entropy of reaction that leads to higher values of enthalpy in Fig. 4 in comparison to Gibbs free energy. Fig. 5 also shows the decrease of reaction heat capacity with temperature due to the reduction of the difference in heat capacity between reaction products and reactants.

On the other hand, Fig. 6 shows the oxidation reaction of Eq. 5 of the largest oxygen-deficient cluster. The values of Gibbs free energy and enthalpy are all negative, indicating that the reaction is exergonic and exothermic at all shown temperatures. Unlike Fig. 4, the values of Gibbs free energy in Fig. 6 are all higher than the enthalpy. This is because of the negative values of the entropy as in Fig. 7. Fig. 7 also shows the negative values of the reaction heat capacity due to the decrease of the heat capacity of the reaction products with respect to the reactants.

Figs. 8 and 9 show charges on the largest cluster and charges on reacting gases using natural bond orbitals (NBO) analysis. As we can see from Fig. 8 that oxygen atoms have negative charges. These charges attract positive charges on gases. As a result, C atom in CO gas and H atoms in NH₃ and CH₄ gases all will be attracted to O atoms in the Cr₆O₁₈ cluster. Although hydrogen atoms in isolated H₂ molecules have no charges, they acquire charge as they approach CrO₃ clusters. The nearest H atom (to O atoms in Cr₆O₁₈ cluster) acquire a positive charge while the far one

acquires a negative charge. The same is true for O₂ molecules that approaches oxygen-deficient clusters.

Fig. 10 shows the relative sensitivity of the Cr₆O₁₈ cluster to hydrogen, as described by Eq. 10. The sensitivity increases as the temperature increases. The highest sensitivity is limited by power consumption and structural changes in the sensitive material.

Table 1 shows the thermodynamic quantities of the reactions in Eqs. (1-5) at standard conditions (temperature 298.15 Kelvin and pressure 1 atm). As we can see that all Gibbs free energy of reactions are positive. This means that all the reactions are exergonic (spontaneous). However, the first and last reactions in Table 1 are the only exothermic reactions as determined by the values of the enthalpy. The rest of the reactions are endothermic. Therefore, some gas sensors need a heating source to maintain high temperature while others do not need this source.

The change in entropy of a reaction depends on several factors. Molecules with higher kinetic energy have higher disorder and entropy. Entropy also increases as the number of molecules increase. The first two reactions have no change in the number of molecules. However, the exergonic reactions that add energies to the reaction products increase entropy. The third and fourth reactions have an increase in the number of product molecules. The result is a high entropy change due to the increase in the number of molecules and exergonic reactions. The last reaction shows the reverse of the changes in the first four reactions. The number of molecules of the products is half of that of the reactants that result in a reduction of entropy despite the increase of the kinetic energy of the products. The values of heat capacity are related to entropy and show the same variation in Table 1.

The term $\exp(E_{ga}-E_{gg})$ in Eq. 9, when applied to the various considered reactions, will produce the value 4.487 eV due to reduction or increase in the energy gap. This change of the energy gap by more than one electron Volt is typical in gas sensors. On the other hand, the values of the Gibbs free energy in Table 1 shows that the recovery time of re-oxidation in Eq. 5 is smaller than the response time of all the considered gases.

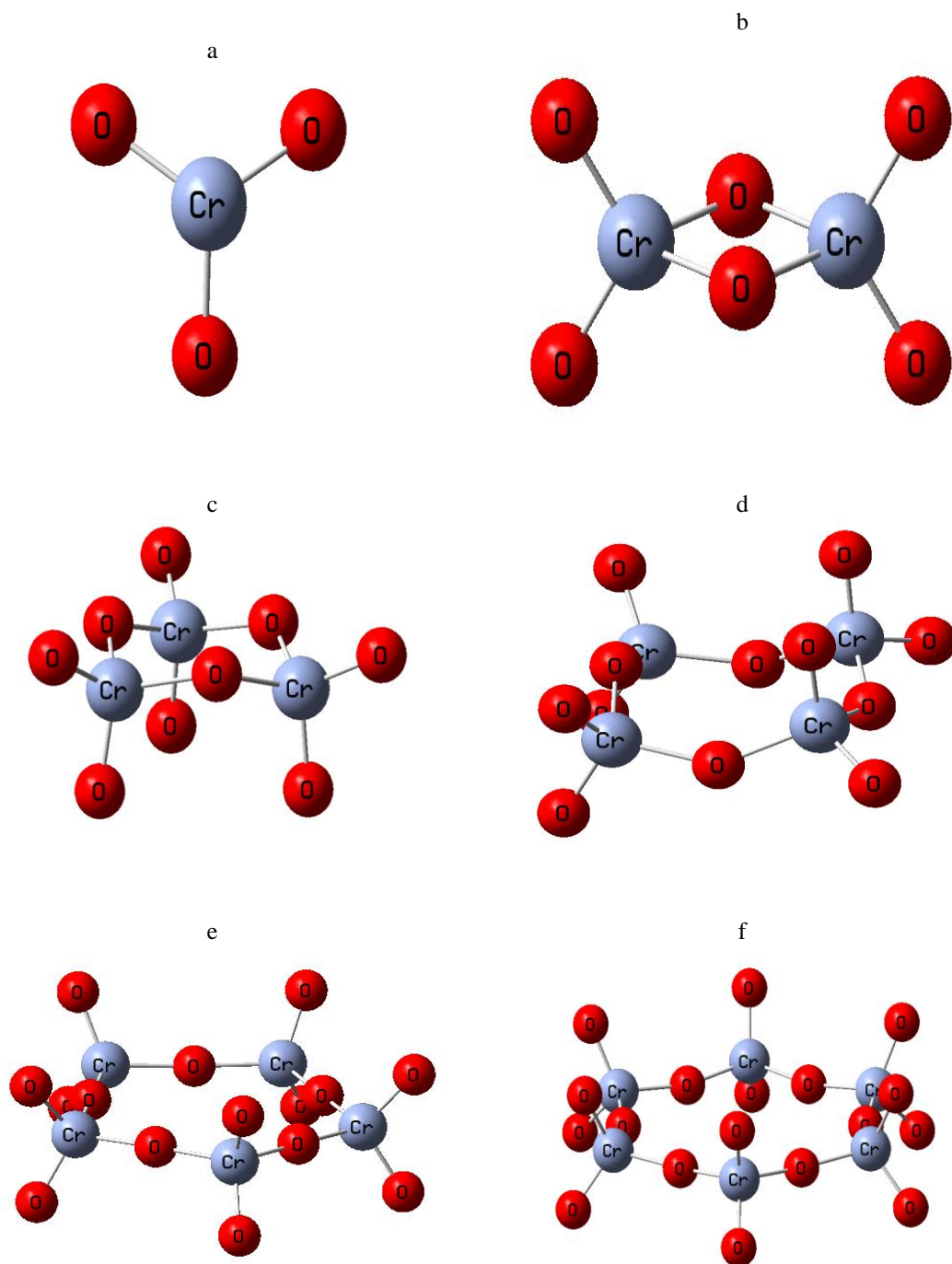


Fig. 1: Smallest chromium trioxide clusters, i.e. (a) CrO_3 , (b) Cr_2O_6 , (c) Cr_3O_9 , (d) Cr_4O_{12} , (e) Cr_5O_{15} and (f) Cr_6O_{18} . These clusters are geometrically optimized using B3LYP hybrid density functional theory.

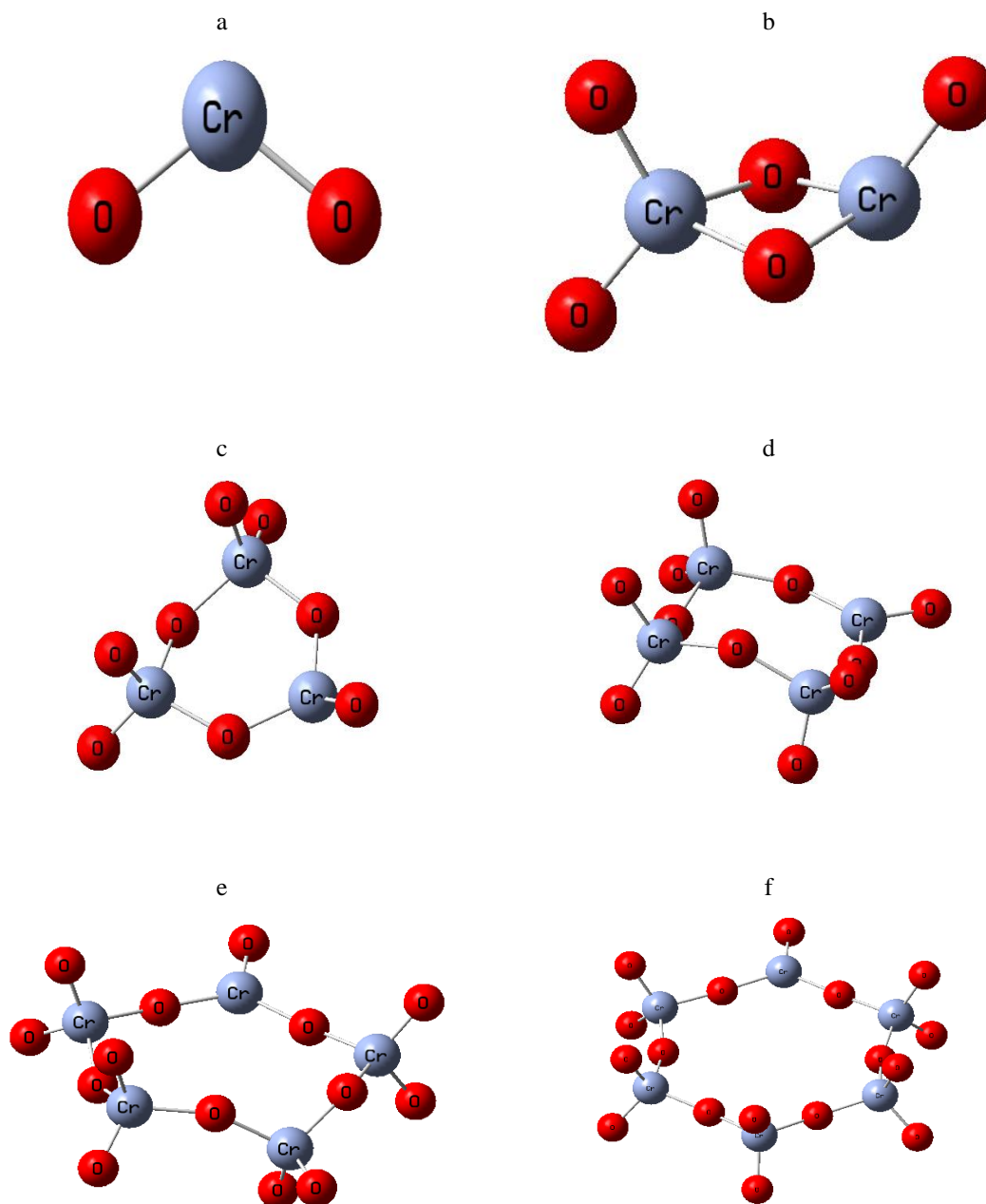


Fig. 2: Smallest chromium trioxide clusters with one O atom deficiency, i.e. (a) CrO_2 , (b) Cr_2O_5 , (c) Cr_3O_8 , (d) Cr_4O_{11} , (e) Cr_5O_{14} and (f) Cr_6O_{17} . These clusters are geometrically optimized using B3LYP hybrid density functional theory.

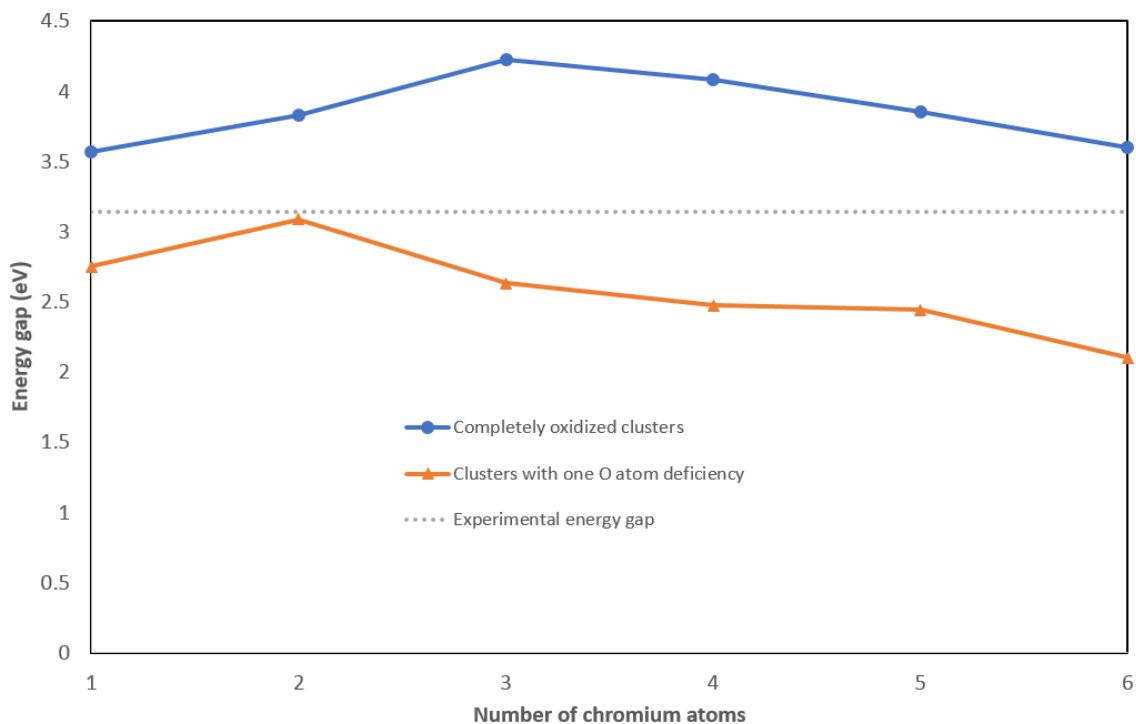


Fig. 3: The variation of the energy gap of $(CrO_3)_n$ clusters. The energy gap of one O atom deficient clusters is also shown. The recommended bulk experimental gap of CrO_3 is also shown [1].

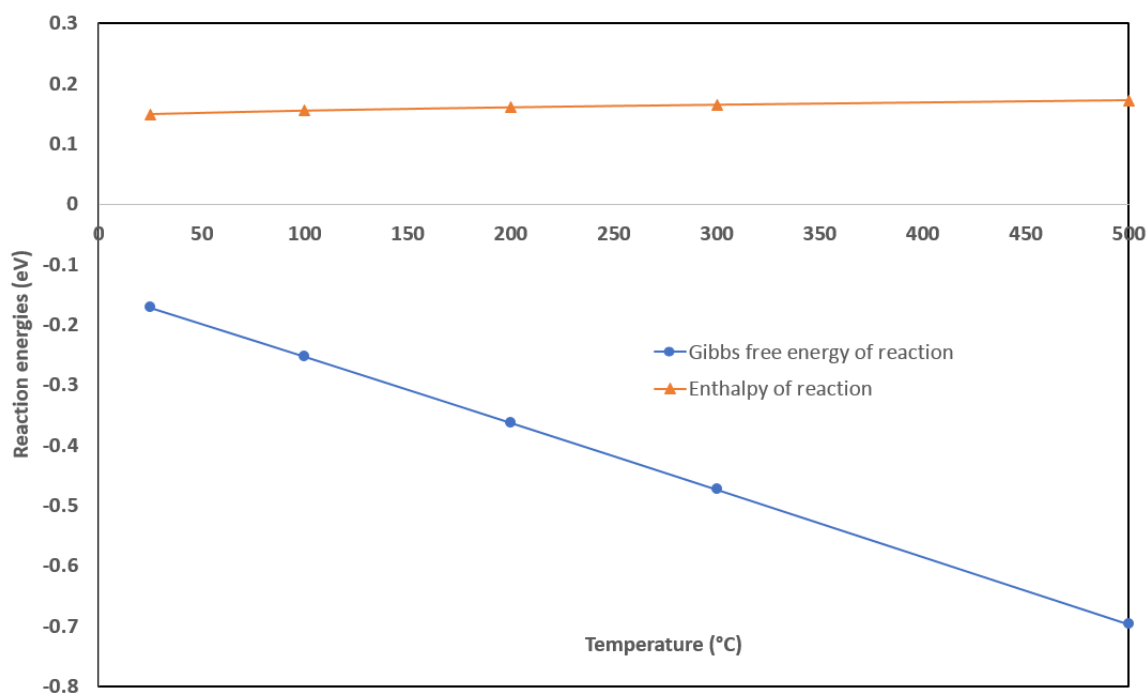


Fig. 4: Gibbs free energy and enthalpy of the reaction of H_2 molecule with the largest CrO_3 investigated cluster of Eq. 2 as a function of temperature.

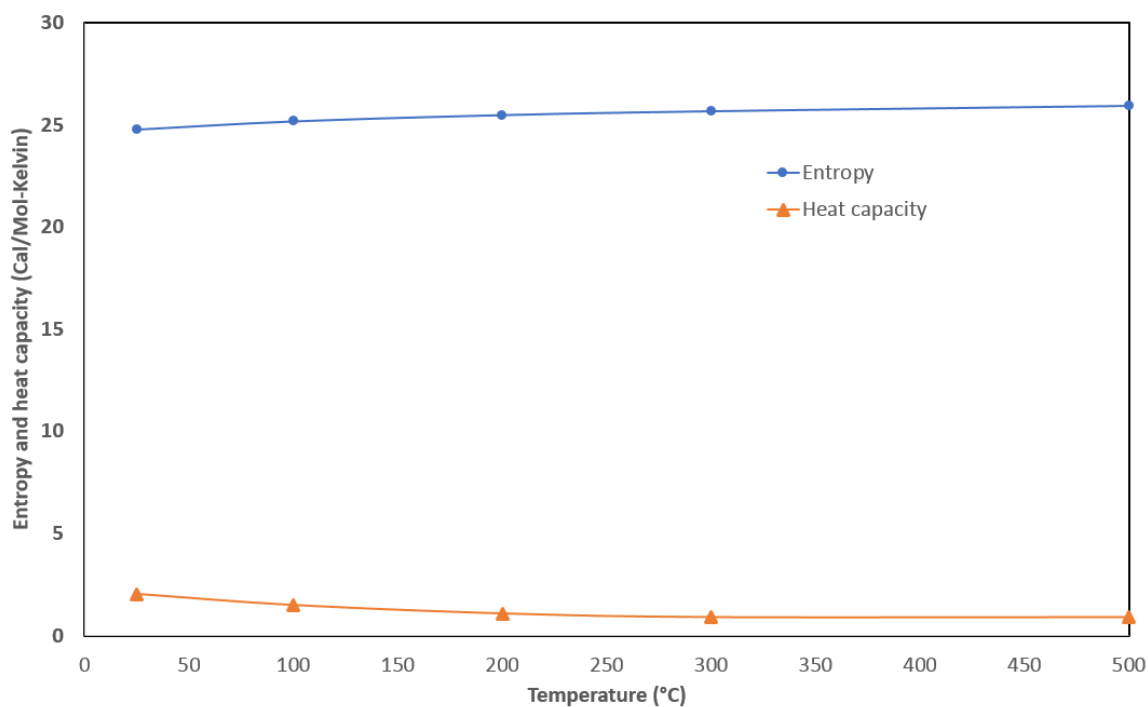


Fig. 5: Entropy and heat capacity of the reaction of H₂ molecule with the largest CrO₃ investigated cluster of Eq. 2 s a function of temperature.

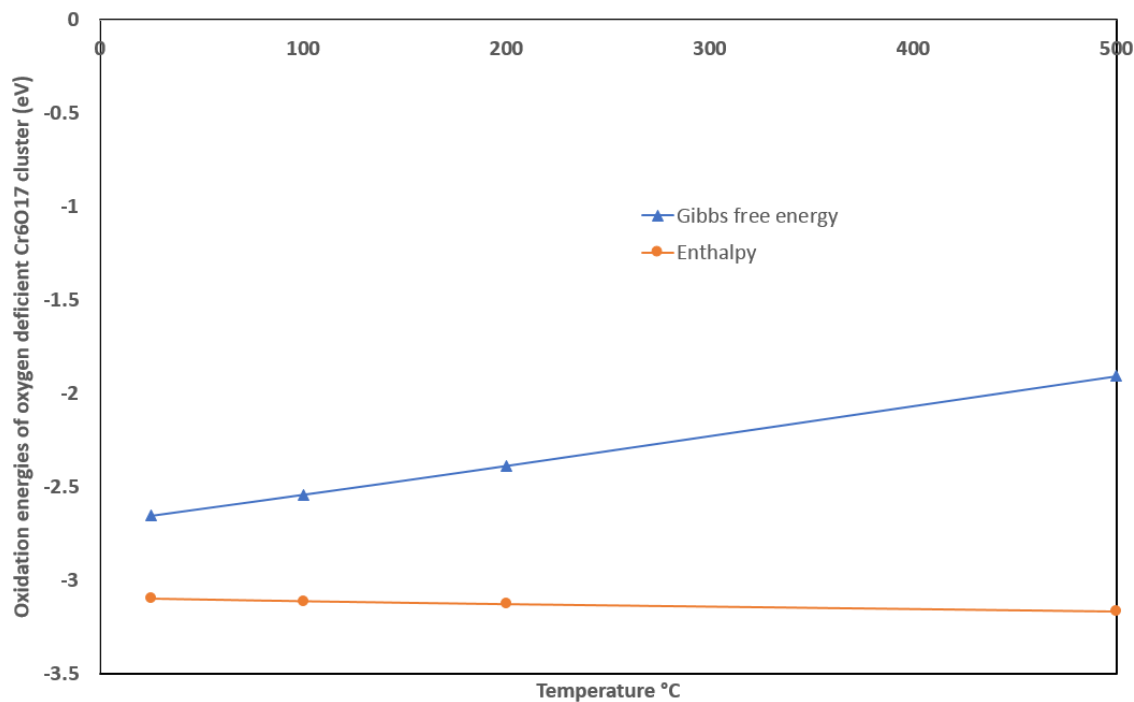


Fig. 6: Gibbs free energy and enthalpy of the reaction of O₂ molecule with oxygen-deficient largest CrO₃ investigated cluster of Eq. 5 as a function of temperature.

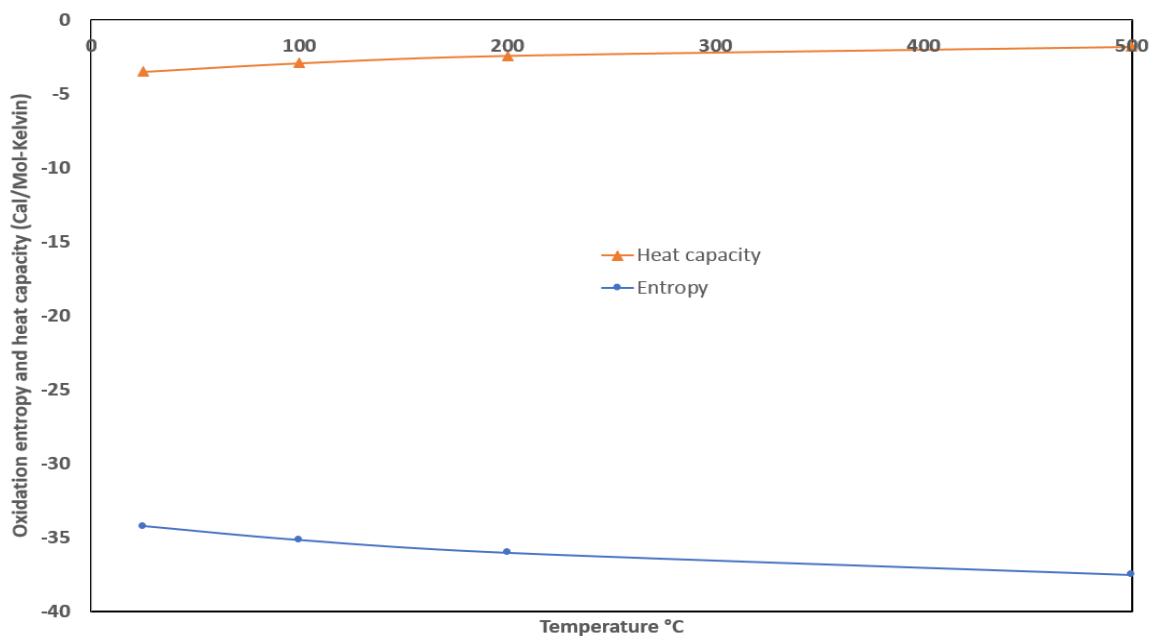


Fig. 7: Entropy and heat capacity of the reaction of O₂ molecule with oxygen-deficient largest CrO₃ investigated cluster of Eq. 5 as a function of temperature.

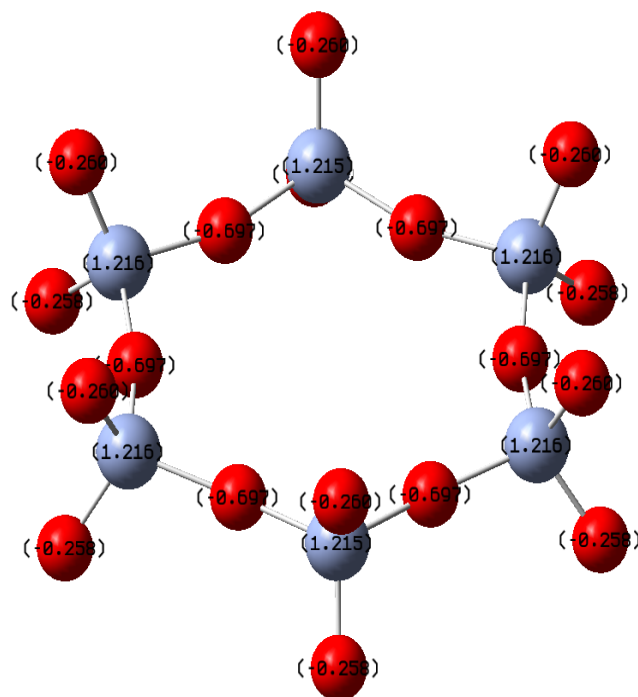


Fig. 8: NBO charges on the largest CrO₃ investigated cluster.

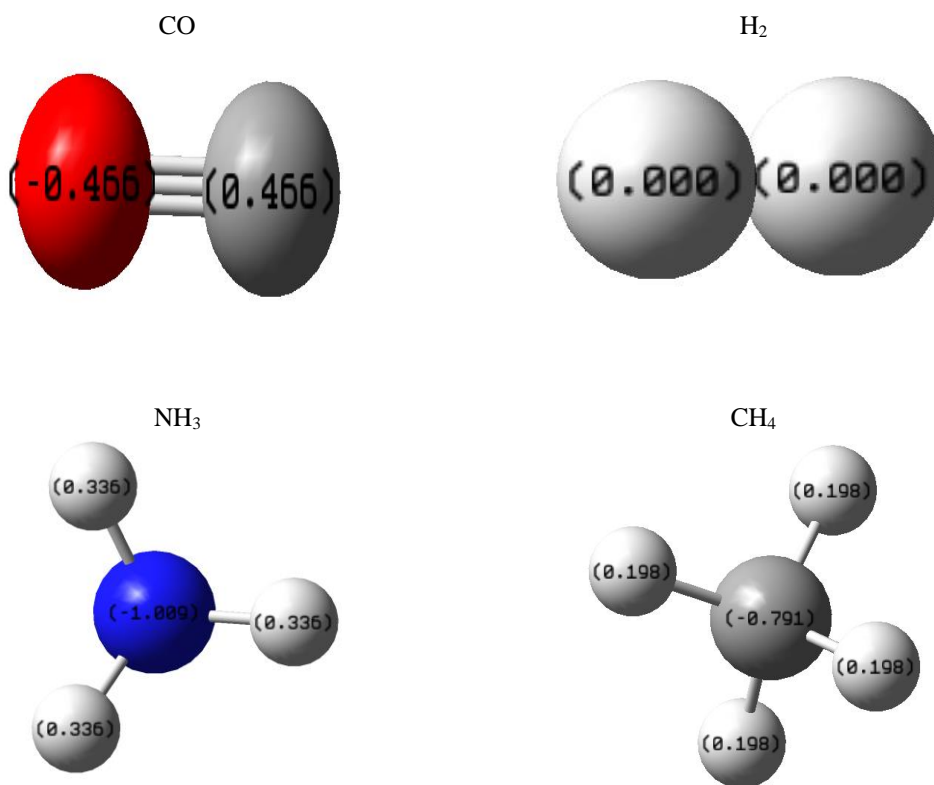


Fig. 9: NBO charges on the four considered molecules CO, H₂, NH₃, and CH₄.

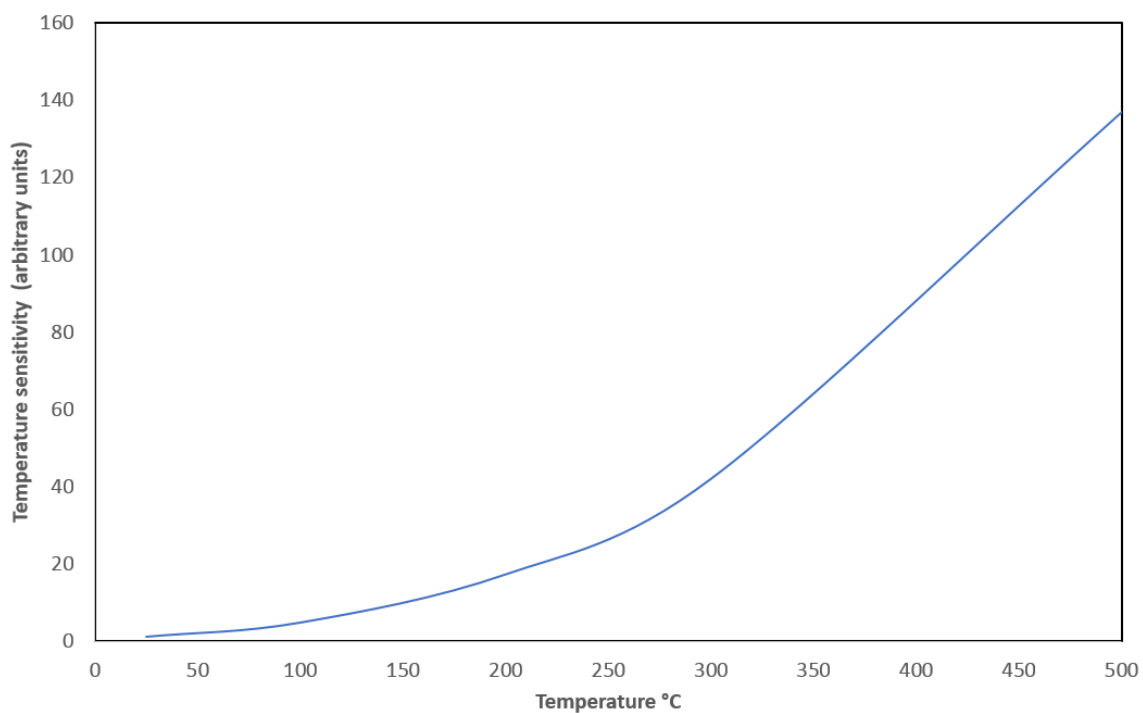


Fig. 10: Temperature sensitivity of the reaction $\text{Cr}_6\text{O}_{18} + \text{H}_2 \rightarrow \text{Cr}_6\text{O}_{17} + \text{H}_2\text{O}$.

Table 1: The thermodynamic quantities of interacting gases with the largest CrO₃ cluster (Cr₆O₁₈) are shown in this table at standard temperature and pressure (temperature 298.15 Kelvin and pressure 1 atm).

	Reaction	ΔG (eV)	ΔH (eV)	ΔS (cal/mol-K)	ΔC_v (cal/mol-K)
1	$\text{Cr}_6\text{O}_{18} + \text{CO} \rightarrow \text{Cr}_6\text{O}_{17} + \text{CO}_2$	-0.906	-0.716	14.695	2.874
2	$\text{Cr}_6\text{O}_{18} + \text{H}_2 \rightarrow \text{Cr}_6\text{O}_{17} + \text{H}_2\text{O}$	-0.171	0.149	24.788	2.012
3	$3/2\text{Cr}_6\text{O}_{18} + \text{NH}_3 \rightarrow 3/2\text{Cr}_6\text{O}_{17} + 1/2\text{N}_2 + 3/2\text{H}_2\text{O}$	-0.123	0.635	58.613	6.607
4	$4\text{Cr}_6\text{O}_{18} + \text{CH}_4 \rightarrow 4\text{Cr}_6\text{O}_{17} + \text{CO}_2 + 2\text{H}_2\text{O}$	-0.077	1.670	135.170	16.310
5	$2\text{Cr}_6\text{O}_{17} + \text{O}_2 \rightarrow 2\text{Cr}_6\text{O}_{18}$	-5.311	-6.196	-68.465	-6.962

4. Conclusions

The thermodynamic quantities of the interaction of CO, H₂, NH₃, CH₄ with CrO₃ clusters at standard conditions are calculated using density functional theory. These gases pick up oxygen atoms from the oxygen saturated CrO₃ clusters. The calculated thermodynamic quantities show that all reactions are exergonic at standard conditions (spontaneous) due to the negative sign of the Gibbs free energy. However, not all the reactions are exothermic due to the positive values of the reaction enthalpies for some of the gases. The reactions can proceed in high values of temperature depending on Gibbs free energy and enthalpy. The entropy of these reactions can decide what reaction needs additional heating to proceed. Positively charged atoms in gases are attracted to the negatively charged oxygen atoms that can be calculated using NBO analysis. The temperature dependence of sensitivity can be calculated using reaction rates which is a function of Gibbs free energy.

References

- [1] Z.M. Hanafi, F.M. Ismail, A.K. Mohamed, X-ray photoelectron spectroscopy of chromium trioxide and some of its suboxides, *Zeitschrift Fur Physikalische Chemie*. 194 (1996) 61–67. https://doi.org/10.1524/zpch.1996.194.part_1.061.
- [2] P. Rubio-Pereda, G.H. Cocolletzi, Reactivity of phosphorene with a 3d element trioxide (CrO₃) considering van der Waals molecular interactions: a DFT-D2 study, *Journal of Molecular Modeling*. 23 (2017). <https://doi.org/10.1007/s00894-017-3225-z>.
- [3] I.Y. Mittova, V. V. Pukhova, O.A. Pinyaeva, A.A. Emel'yanova, GaAs Thermal Oxidation by Introducing CrO₃ into a Gaseous Oxidizer, *Russian Microelectronics*. 30 (2001) 106–110. <https://doi.org/10.1023/A:1009433927773>.
- [4] J. Tian, J. Zhao, Q. Xue, Effect of oxidizer CrO₃ on lubrication performance of MoS₂, *Mocaxue Abdulsttar et al., 2022*
- Xuebao/Tribology. 18 (1998) 279–282.
- [5] G.P. Singh, S. Ram, J. Eckert, H.J. Fecht, Synthesis and morphological stability in CrO₂ single crystals of a half-metallic ferromagnetic compound, in: *Journal of Physics: Conference Series*, Institute of Physics Publishing, 2009: p. 012110. <https://doi.org/10.1088/1742-6596/144/1/012110>.
- [6] H.J. Zhai, S. Li, D.A. Dixon, L.S. Wang, Probing the electronic and structural properties of chromium oxide clusters (CrO₃)_n- and (CrO₃)_n (n = 1-5): Photoelectron spectroscopy and density functional calculations, *Journal of the American Chemical Society*. 130 (2008) 5167–5177. <https://doi.org/10.1021/ja077984d>.
- [7] V.Z. Fridman, R. Xing, Investigating the CrO_x/Al₂O₃ dehydrogenation catalyst model: II. Relative activity of the chromium species on the catalyst surface, *Applied Catalysis A: General*. 530 (2017) 154–165. <https://doi.org/10.1016/j.apcata.2016.11.024>.
- [8] Ø. Espelid, K.J. Børve, V.R. Jensen, Structure and thermodynamics of gaseous oxides, hydroxides, and mixed oxohydroxides of chromium: CrO_m(OH)_n (m, n = 0-2) and CrO₃. A computational study, *Journal of Physical Chemistry A*. 102 (1998) 10414–10423. <https://doi.org/10.1021/jp9830427>.
- [9] E.B. Rudnyi, O.M. Vovk, E.A. Kaibicheva, L.N. Sidorov, Formation enthalpies of oxygen-containing anions of group VI elements in the gas phase and the electron affinities of CrO₃, MoO₃, and WO₃, *The Journal of Chemical Thermodynamics*. 21 (1989) 247–258. [https://doi.org/10.1016/0021-9614\(89\)90014-1](https://doi.org/10.1016/0021-9614(89)90014-1).
- [10] K. Yoshii, Spin rotation, glassy state, and magnetization switching in R CrO₃ (R = La1-xPrx, Gd, and Tm): Reinvestigation of magnetization reversal, *Journal of Applied Physics*. 126 (2019). <https://doi.org/10.1063/1.5116205>.

- [11] D. Han, M. Bouras, C. Botella, A. Benamrouche, B. Canut, G. Grenet, G. Saint-Girons, R. Bachelet, Poisson ratio and bulk lattice constant of (Sr_{0.25}La_{0.75})CrO₃ from strained epitaxial thin films, *Journal of Applied Physics*. 126 (2019). <https://doi.org/10.1063/1.5101049>.
- [12] S. Khaldi, Z. Dibi, Neural Network Technique for Electronic Nose Based on High Sensitivity Sensors Array, *Sensing and Imaging*. 20 (2019). <https://doi.org/10.1007/s11220-019-0233-3>.
- [13] C. Wang, L. Yin, L. Zhang, D. Xiang, R. Gao, Metal oxide gas sensors: Sensitivity and influencing factors, *Sensors*. 10 (2010) 2088–2106. <https://doi.org/10.3390/s100302088>.
- [14] A. Omidvar, Indium-doped and positively charged ZnO nanoclusters: versatile materials for CO detection, *Vacuum*. 147 (2018) 126–133. <https://doi.org/10.1016/j.vacuum.2017.10.023>.
- [15] Joseph W. Ochterski, *Thermochemistry in Gaussian*, (2000).
- [16] X. Zhou, L. Yang, Y. Bian, Y. Wang, N. Han, Y. Chen, Improving the signal resolution of semiconductor gas sensors to high-concentration gases, *Solid-State Electronics*. 162 (2019) 107648. <https://doi.org/10.1016/j.sse.2019.107648>.
- [17] Q. Zhou, W. Zeng, W. Chen, L. Xu, R. Kumar, A. Umar, High sensitive and low-concentration sulfur dioxide (SO₂) gas sensor application of heterostructure NiO-ZnO nanodisks, *Sensors and Actuators, B: Chemical*. 298 (2019). <https://doi.org/10.1016/j.snb.2019.126870>.
- [18] H. An, M. Yoo, H. Ha, H. Choi, E. Kang, H.Y. Kim, Efficient Sn Recovery from SnO₂ by Alkane (C_xH_y=2x+2, 0 ≤ x ≤ 4) Reduction, *Scientific Reports*. 9 (2019). <https://doi.org/10.1038/s41598-019-53389-7>.
- [19] F. Salles, H. Jobic, G. Maurin, M.M. Koza, P.L. Llewellyn, T. Devic, C. Serre, G. Ferey, Experimental evidence supported by simulations of a very high H₂ diffusion in metal organic framework materials, *Physical Review Letters*. 100 (2008). <https://doi.org/10.1103/PhysRevLett.100.245901>.
- [20] A. Mirzaei, J.H. Kim, H.W. Kim, S.S. Kim, How shell thickness can affect the gas sensing properties of nanostructured materials: Survey of literature, *Sensors and Actuators, B: Chemical*. 258 (2018) 270–294. <https://doi.org/10.1016/j.snb.2017.11.066>.
- [21] M. J. Frisch, G. W. Trucks, H. B. Schlegel, B.M. M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, H.P.H. G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, M.H. A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, T.N. M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, J. Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, E.B. J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, J.N. K. N. Kudin, V. N. Staroverov, R. Kobayashi, J.T. K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J.B.C. M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, R.E.S. V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, J.W.O. O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, G.A.V. R. L. Martin, K. Morokuma, V. G. Zakrzewski, A.D.D. P. Salvador, J. J. Dannenberg, S. Dapprich, J.C. O. Farkas, J. B. Foresman, J. V. Ortiz, and D.J. Fox, *Gaussian 09*, (2009).
- [22] M.A. Khillia, A.A. Hanna, Electrical properties of semiconductor materials. Chromium trioxide, *Thermochemica Acta*. 51 (1981) 335–341. [https://doi.org/10.1016/0040-6031\(81\)85171-4](https://doi.org/10.1016/0040-6031(81)85171-4).