

Advanced Statistical Mechanics Coursework

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Please note that due to unforeseen circumstances, there was not enough time to complete Question 5 on the assessment brief. This assessment therefore consists of answers to questions 1-4 only. Please also be aware that there seems to have been (a) mistake(s) in earlier parts of the coursework. Therefore, the assessment has been completed by carrying the results from question 2 all the way through and commenting on subsequent results and plots.

QUESTION 1

Take the following equation

$$K = \frac{Q_{CO_2}}{(Q_{O_2})^{1/2} Q_{CO}} \quad (1)$$

where

$$Q_i = q_i^{trans} q_i^{rot} q_i^{vib} \quad (2)$$

and thus

$$K = \frac{q_{CO_2}^{trans} q_{CO_2}^{rot} q_{CO_2}^{vib}}{(q_{CO}^{trans} q_{CO}^{rot} q_{CO}^{vib})(q_{O_2}^{trans} q_{O_2}^{rot} q_{O_2}^{vib})^{1/2}} \quad (3)$$

Now note that

$$q_i^{trans} = V \left(\frac{2\pi m_i k_B T}{h^2} \right)^{3/2} \quad (4)$$

Therefore,

$$K = V^{-1/2} \left(\frac{h^2}{2\pi k_B T} \right)^{3/4} \left(\frac{m_{CO_2}}{m_{CO}(m_{O_2})^{1/2}} \right)^{3/2} \frac{q_{CO_2}^{rot} q_{CO_2}^{vib}}{(q_{CO}^{rot} q_{CO}^{vib}) \times (q_{O_2}^{rot} q_{O_2}^{vib})^{1/2}} \times e^{(-\Delta E/k_B T)} \quad (5)$$

Note that $\Delta E = E_{CO_2} - E_{CO} - \frac{1}{2}E_{O_2}$ where $E_{CO_2} = \frac{1}{2}E_{O_2} = 0$

Given that

$$V = \frac{k_B T}{P^\circ} \quad (6)$$

$$K = \left(\frac{P^\circ}{k_B T} \right)^{1/2} \left(\frac{h^2}{2\pi k_B T} \right)^{3/4} \left(\frac{m_{CO_2}}{m_{CO}(m_{O_2})^{1/2}} \right)^{3/2} \frac{q_{CO_2}^{rot} q_{CO_2}^{vib}}{(q_{CO}^{rot} q_{CO}^{vib}) \times (q_{O_2}^{rot} q_{O_2}^{vib})^{1/2}} \times e^{(-\Delta E/k_B T)} \quad (7)$$

Now introduce the equation

$$K = \frac{Q_{CO_2}}{(Q_{O_2})^{1/2} Q_{CO}} = \frac{\alpha_{CO_2}}{\alpha_{CO}(\alpha_{O_2})^{1/2}} \quad (8)$$

where

$$\alpha_i = \frac{P_i}{P^\circ} \quad (9)$$

Such that the expression for the equilibrium constant K_P can be written as

$$K_P = \frac{P_{CO_2}}{P_{CO}(P_{O_2})^{1/2}} = \left(\frac{P^\circ}{k_B T} \right)^{1/2} \left(\frac{h^2}{2\pi k_B T} \right)^{3/4} \left(\frac{m_{CO_2}}{m_{CO}(m_{O_2})^{1/2}} \right)^{3/2} \frac{q_{CO_2}^{rot} q_{CO_2}^{vib}}{(q_{CO}^{rot} q_{CO}^{vib}) \times (q_{O_2}^{rot} q_{O_2}^{vib})^{1/2}} \times e^{(-\Delta E/k_B T)} \quad (10)$$

QUESTION 2

Please note that for this question, the used constants and performed calculations can be found in the Python file titled *ASM Q2*.

For completeness, the vibrational part of the partition function is calculated as follows:

$$q_i^{vib} = \prod_j \frac{\exp(-0.5 \times c \times h \times v)}{1 - \exp(-c \times h \times v)} \quad (11)$$

and where the rotational part of the partition function is calculated by

$$q_i^{rot} = \frac{2k_B T}{h^2} \frac{I_i}{\sigma_i} \quad (12)$$

The partial pressure of CO_2 is then calculated by rearranging equation (10) to give

$$P_{CO_2} = P_{CO} \times (P_{O_2})^{1/2} \times \left(\frac{P^\circ}{k_B T} \right)^{1/2} \left(\frac{h^2}{2\pi k_B T} \right)^{3/4} \left(\frac{m_{CO_2}}{m_{CO}(m_{O_2})^{1/2}} \right)^{3/2} \frac{q_{CO_2}^{rot} q_{CO_2}^{vib}}{(q_{CO}^{rot} q_{CO}^{vib}) \times (q_{O_2}^{rot} q_{O_2}^{vib})^{1/2}} \times e^{(-\Delta E/k_B T)} \quad (13)$$

Running this calculation for the constants as given on the assessment brief, the partial pressure of CO_2 is found to be 9.3319×10^5 Pa, which equals 9.3319 bar and seems unusually high. Given the partial pressures of CO and O_2 , one would assume that the molar fraction of CO_2 would be roughly 0.99999994 and therefore the partial pressure of CO_2 would, in an ideal gas, be around 0.299999982 bar. Therefore, the result for this calculation is approximately 30 times too large. If these numbers would be correct, it would suggest that the reaction is not actually ran at chemical equilibrium. Even with some of the gas being inert, the current numbers are still off. Since the assessment brief states that the reaction is in fact run at equilibrium, the calculated partial pressure suggests that an error has been made somewhere in the calculations.

QUESTION 3

Please note that for this question, the used constants and performed calculations can be found in the Python file titled *ASM Q3*.

Using the equations as given in Appendix A, the reaction rates are as follows

$$\begin{aligned} k_{O_2ads}^{fwd} &= 0.00017642792810036717 \\ k_{O_2ads}^{rev} &= 5.00969114578702e + 18 \\ k_{COads}^{fwd} &= 0.14937796998669126 \\ k_{COads}^{rev} &= 73.60869608404262 \\ k_{COoxi}^{fwd} &= 1568579.9315430296 \\ k_{COoxi}^{rev} &= 5.797482920696401e - 14 \end{aligned}$$

Thus, the expression

$$\left(\frac{k_{O_2ads}^{fwd}}{k_{O_2ads}^{rev}} \right)^{1/2} \frac{k_{COads}^{fwd}}{k_{COads}^{rev}} \frac{k_{COoxi}^{fwd}}{k_{COoxi}^{rev}} \quad (14)$$

will lead to

$$\left(\frac{0.00017642792810036717}{5.00969114578702e + 18} \right)^{1/2} \frac{0.14937796998669126}{73.60869608404262} \frac{1568579.9315430296}{5.797482920696401e - 14} \approx 3.258e + 05 \quad (15)$$

At chemical equilibrium, this rate constant for the formation of CO_2 should be around 1. This is because at equilibrium, every elementary reaction and its reverse occur at the same net rate. This means that the ratio of forward to reverse rate constants, scaled according to stoichiometry, must exactly balance so there is no net flux of any species. Clearly, the obtained result is much larger than 1 and therefore suggests that this reaction is either not at chemical equilibrium, or a mistake has been made along the way. Knowing the reaction conditions should lead to chemical equilibrium, it is extremely likely that the result to this question is simply a mistake carried on as a result of the answer obtained for question 2.

QUESTION 4

Please note that for each of the three simulations, the Zacros and Python plotting files can be found in their corresponding folder within the *ASM Q4* folder.

The Kinetic Monte Carlo simulations were run for the parameters as given by question four. This resulted in three graphs that show the trajectory of CO* and O* coverages over time for each of the different random seeds. These graphs can be found in Figure 1, 2 and 3 respectively.

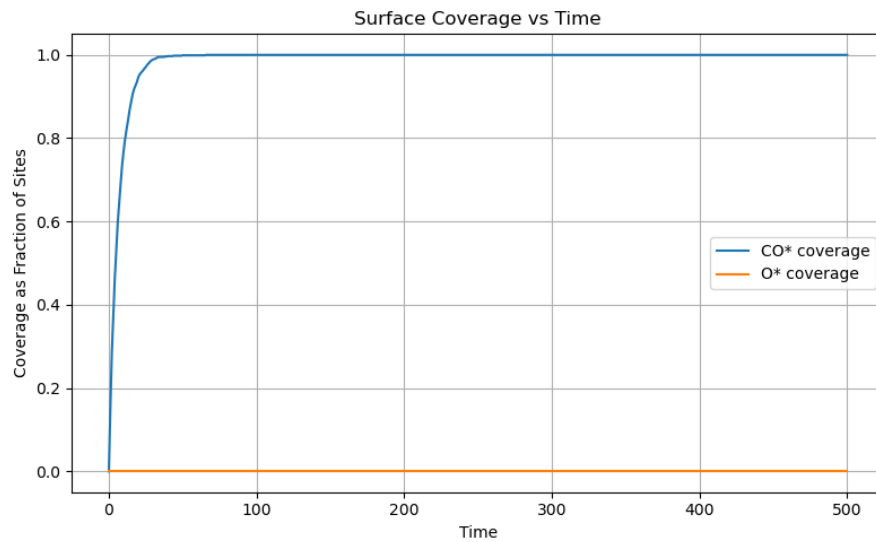


Figure 1: Surface Coverage over Time - Simulation 1

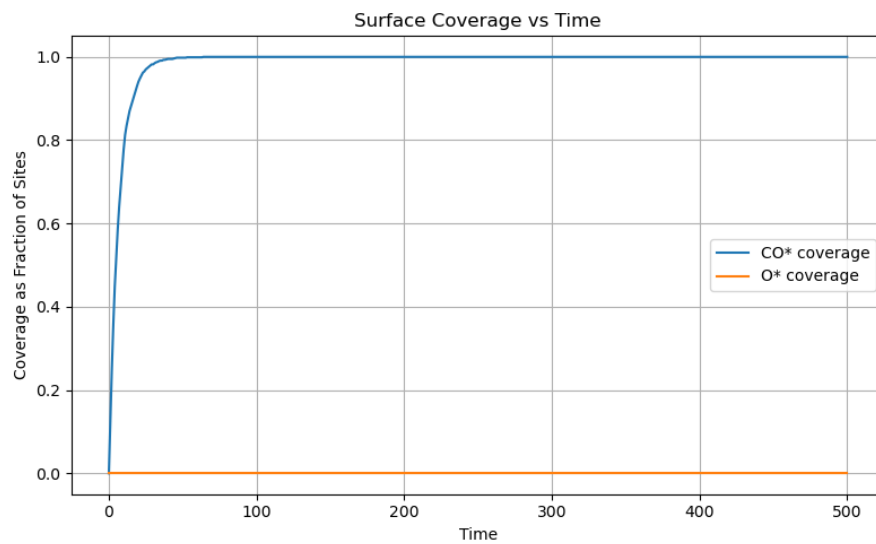


Figure 2: Surface Coverage over Time - Simulation 2

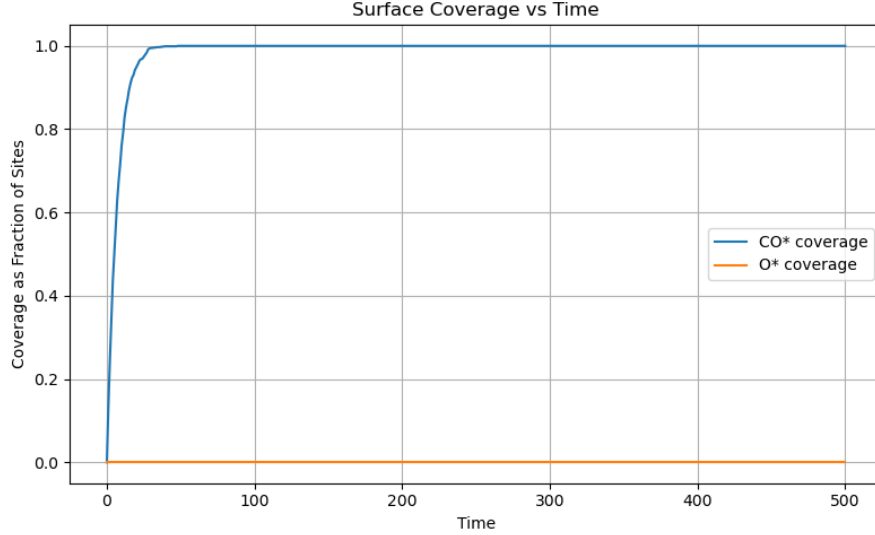


Figure 3: Surface Coverage over Time - Simulation 3

From the plots in Figure 1, 2 and 3, two things become apparent:

- At $t = 0$, both CO^* and O^* coverages are zero as the lattice was empty. However, because the CO adsorption barrier is effectively zero and its forward prefactor is extremely large, even at a CO partial pressure of only $20ppb$, CO molecules begin to stick to the surface almost immediately. In practice, within a few microseconds, the first handful of CO adsorption events convert vacant sites into CO^* . As soon as there are a few CO^* adsorbate molecules present, they consume any remaining single vacancies that appear by desorption or diffusion. Because the lattice is $40 \times 25 = 1000$ sites, it only takes a small fraction of those sites being filled for CO adsorption to proceed even faster. After all, each newly filled CO^* slightly increases the rate at which additional CO molecules find adjacent empty spots. As a result, by $t \approx 10s$ the CO^* coverage curve is already above 0.9 (i.e. 900 out of 1000 sites filled). Within tens of seconds, CO^* reaches essentially a surface coverage of 100% and producing a 'flatline' for the remainder of the simulation.
- Although O_2 adsorption and dissociation onto two neighbouring sites is part of the mechanism, the O_2 forward prefactor is about three orders of magnitude smaller than the CO adsorption value. Moreover, O_2 must find two adjacent vacancies at once to adsorb. This requirement becomes increasingly unlikely once CO^* begins occupying sites. Because CO^* covers almost the entire lattice in the first few seconds, O_2 never gets the opportunity to land on two empty sites. Even if a pair of adjacent sites momentarily appears, CO would immediately reoccupy those sites long before a second vacancy could appear for O_2 to disassociate. Consequently, the O^* surface coverage curve stays around 0 as no O^* has a chance to accumulate on the surface.

Next, graphs were plotted to show the number of molecules of all three gas phase species that are being produced or consumed. These graphs can be found in Figure 4, 5 and 6 respectively.

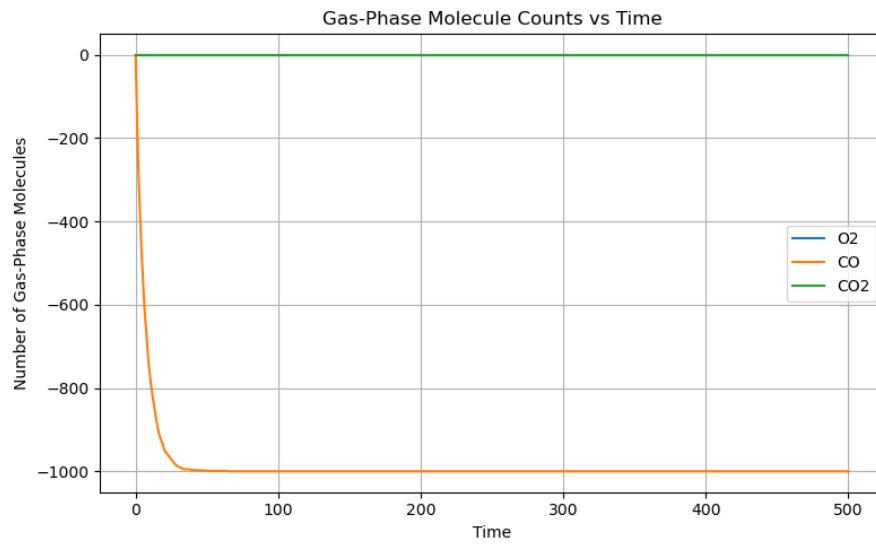


Figure 4: Gas-Phase Counts over Time - Simulation 1

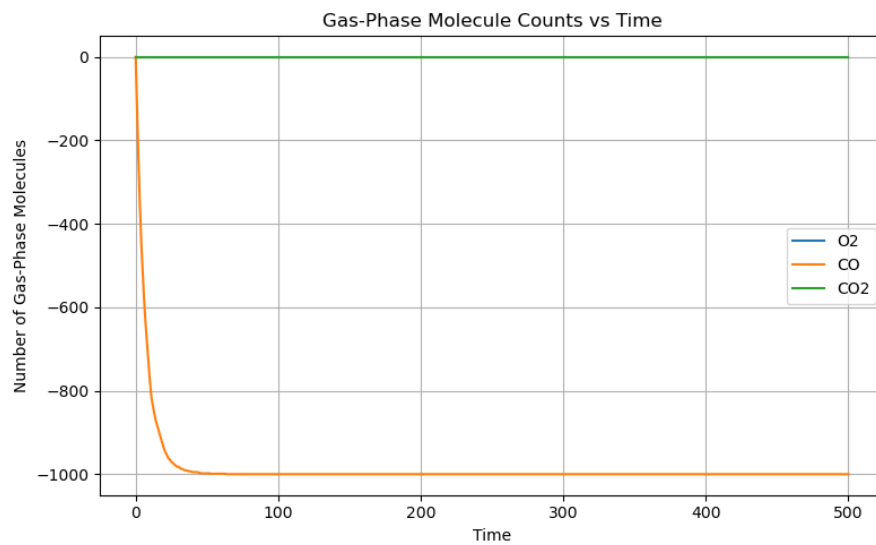


Figure 5: Gas-Phase Counts over Time - Simulation 2

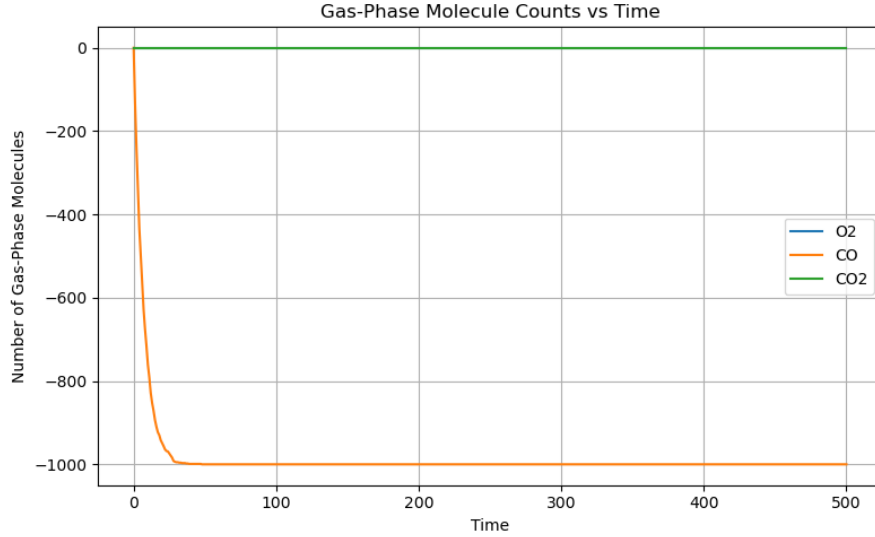


Figure 6: Gas-Phase Counts over Time - Simulation 3

What these graphs show is the time evolution of gas-phase species under equilibrium conditions. The CO trace becomes greatly negative almost immediately, reflecting rapid CO adsorption to fill the 1000 catalytic sites. By $t \approx 30\text{s}$, no further CO can be adsorbed, so the CO line on the graph levels off. The O_2 trace is identically zero, just like the CO_2 line. This indicates that dissociative O_2 adsorption never occurs once CO^* dominates the surface. Consequently, CO_2 remains at zero throughout the 500 s because no O^* is ever available to react with CO^* . Together, these curves confirm that under the chosen equilibrium gas composition, the surface becomes poisoned with CO: CO is consumed until every site is occupied and neither O_2 nor CO_2 participate significantly in the gas-phase after that point.

As expected, there is little to no difference between the three simulations for the two different graphs. This is because there is no difference in these simulations other than a different random seed being used. Therefore, one would expect the simulations to have similar outcomes for each of the different runs.