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Experimental study of the frequency factor for the Polanyi-Wigner equation.

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Abstract

For the first time, an experimental procedure to calculate the frequency factor of the Polanyi-Wigner equation and to study how temperature influences on it is presented. This parameter is necessary to calculate desorption rates for environments where this process occurs. The method presented is based on the analysis of a quartz crystal microbalance signal. In the literature the frequency factor is not experimentally obtained but it is rather assumed as $k_B \cdot T/h$, proposed by the activated state theory for first order desorption processes, or it is estimated by other methods. Additionally, its variation with temperature is not experimentally explored so far.

Two different kind of desorption experiments of zeroth order desorption have been carried out to perform this study. The first experiment, carried out at a constant rate of warming up, is devoted to obtain the desorption energy, which is compared with previous values reported in the literature. The second group of desorption

experiments is performed at constant temperature and is used to calculate and study the frequency factor. Several temperatures have been specifically selected, allowing us to derive the influence of the temperature on this parameter. For ethane, we have calculated an increase of around a 50% for the frequency factor corresponding to an increase in temperature of only 6 K. This result must be taken into account when the Polanyi-Wigner equation is used for calculation purposes.

Key words: ice films, sublimation energy, experimental laboratory

1 Introduction

Desorption experiments are widely performed to study the properties of many materials. From the theoretical point of view, the concepts of desorption and sublimation imply different processes, however, in the literature concerning low temperature ices, both are usually assumed as equivalent (see for example Sandford and Allamandola (1993)).

The process involved in these experiments is governed by the Polanyi-Wigner equation (Polanyi and Wigner (1925)):

$$-\frac{dN}{dt} = A_i \cdot N^i \cdot \exp\left(-\frac{E_{des}}{R \cdot T}\right) \quad (1)$$

where N is the surface coverage of molecules, i is the order of the process, A_i is the frequency factor, $(A_i \cdot N^i)$ is the preexponential factor, E_{des} is the desorption energy, T is the absolute temperature and R is the constant for ideal gases. This study has been later developed by the works of Redhead (1962) and Carter (1962).

Equation 1 is used in several fields: catalysis, chemical reactions, astronomy,

Table 1

Values for the frequency factor A_i used in the literature for desorption processes and their corresponding units. N is the surface coverage widely assumed as 10^{15} molecules cm^{-2} and $A_1 = k_B \cdot T/h$ (for first order desorption). Generally a temperature $T = 50$ K is assumed and then, $A_1 = 10^{12} \text{s}^{-1}$.

Desorption order	$A_i = A_1 \cdot N^{1-i}$	Typical values using $A_1 = 10^{12} \text{s}^{-1}$ and $N = 10^{15} \text{molecule cm}^{-2}$	Range of values reported in the literature	Units
0	$A_0 = A_1 \cdot N$	$10^{12} \cdot 10^{15} = 10^{27}$	10^{25} – 10^{32} a, b, c, d	$\text{molecule cm}^{-2} \text{s}^{-1}$
1	A_1	$10^{12} \cdot 10^0 = 10^{12}$	10^{11} – 10^{15} a, b, d	s^{-1}
2	$A_2 = A_1 \cdot N^{-1}$	$10^{12} \cdot 10^{-15} = 10^{-3}$	10^{-5} – 10^{-1} b, d	$\text{molecule}^{-1} \text{cm}^2 \text{s}^{-1}$
References	a: Acharyya et al. (2007), b: Bisschop et al. (2006) c: Bolina and Brown (2005), d: Collings (2003)			

16 desorption kinetics from different material surfaces specifically oriented, etc.
 17 The parameters involved, can be applied to desorption processes to determine
 18 the sticking coefficient, the surface coverage, the residence time, or the order
 19 of the process for a molecule. This latter is related to the kinetics of a molecule
 20 in an elementary process, being usually an integer $i = 0, 1, 2, \dots$, but some
 21 authors, have even obtained a non integer number (Brown and Bolina (2007)).

22 Another relevant application is to determine the desorption energy of a species,
 23 E_{des} , which is defined as the heat required to desorb one mole of a substance.
 24 This parameter is important to compute several thermodynamical magnitudes
 25 such as the reticular energy of ionic compounds, the energy of formation in gas

26 phase from the energy of formation in condensed phase, the bonding energy of
27 a molecule with the surface of a specific material, or the sublimation rate r_{des}
28 of molecules from their bulk ice. In the literature, three procedures to obtain
29 E_{des} using the Polanyi-Wigner equation are reported: i) a group of works are
30 based in the use of a linear form of the Polanyi-Wigner equation by taking
31 the natural logarithm in Eq. (1), then, representing $\ln(r_{des})$ versus $1/T$, E_{des}
32 is obtained from its slope (Luna et al. (2014)); ii) in a second group of works,
33 the desorption energy is obtained by fitting directly the curve obtained during
34 thermal programmed desorption (TPD) experiments under UHV conditions,
35 using E_{des} as a fitting parameter. In this case, it is necessary to previously esti-
36 mate a value for the frequency factor (A_i) (Chakradhar (2011)) or taking it as
37 an additional fitting parameter (Muñoz Caro et al. (2010)); iii) the third group
38 of experiments are formed by desorption at 2 or 3 different constant temper-
39 atures implying a constant desorption rate (for each temperature); then the
40 desorption energy is obtained from every experiment, being the mean E_{des}
41 assumed as the representative value for desorption energy (Sandford and Al-
42 lamandola (1993)). It is remarkable that for all the techniques mentioned, a
43 constant value for A_i has been assumed despite in most of processes temper-
44 ature is not constant and knowing that A_i depends on temperature, as it is
45 declared in the activated state theory (Galwey and Brown (2002)). Therefore,
46 some authors propose to determine A_i for each species under the specific con-
47 ditions for each experiment, but this study has not been done since it implies
48 some previous additional experiments.

49 Due to this lack of studies, one additional application of the Polanyi-Wigner
50 equation is to determine how temperature influences the frequency factor (not
51 experimentally explored so far). Then, it is interesting to study this variation

52 with temperature for different substances to know whether the general assump-
53 tion, used in the literature, of a negligible variation of A_i with temperature is
54 reasonable.

55 From Eq. 1, it is possible to infer that units of A_i depends on the order of the
56 process involved, therefore the same must be taken into account for the mean-
57 ing of this parameter. For a first order desorption process, A_1 can be related
58 to the lattice vibrational frequency of the molecule within its position in the
59 matrix (Sandford and Allamandola (1990); Bisschop et al. (2006); Krongauz
60 (2007)). In the case of atoms or small molecules following a first order process,
61 this factor is assumed to follow the expression $A_1 = k_B \cdot T \cdot h^{-1}$ (Galwey and
62 Brown (2002)), where k_B is the Boltzman constant, h is the Planck constant
63 and T is the absolute temperature. Therefore, this parameter is temperature
64 dependant. Nevertheless in the literature, for all the molecules, the frequency
65 factor (for a first order process) is assumed as $A_1 = 10^{12} \text{ s}^{-1}$, which implies
66 the assumption of a temperature of 50 K regardless the process occurs at an-
67 other different temperature or even in the most common experiments where
68 temperature changes during desorption. For other order processes this param-
69 eter is several orders of magnitude different since it is related to N (surface
70 coverage) and for those cases, it is usually estimated by the authors.

71 The units of A_i are $\text{molecule}^{(1-i)} \text{cm}^{2(i-1)} \text{ s}^{-1}$ (Acharyya et al. (2007)) where i
72 is the order of the process. In Table 1, units and a summary of frequently used
73 values in the literature are reported, where the preexponential factor for zeroth
74 order, has been calculated as follow: $A_0 = A_1 \cdot N$, where N is the surface cov-
75 erage (molecule cm^{-2}). For N , a value of $N = 10^{15} \text{ molecule cm}^{-2}$ is generally
76 used, which implies a surface with perfectly packed spherical particles with a
77 diameter of 3.2 Å. In column 4 can be observed how values calculated or esti-

78 mated for A_i varies even several orders of magnitude for the same desorption
79 order.

80 Despite A_i depends on the molecule desorbing and temperature, no experi-
81 ments are made to study this behaviour. Therefore it is worthy to study the
82 influence of the temperature on this parameter to know whether values usually
83 used are affected by a significant error. This study implies to analyse several
84 desorption experiments at different constant temperatures instead of carrying
85 out desorption experiments where temperature varies continuously.

86 To perform these studies, molecules desorbing can be measured by means
87 three different methods: i) indirectly, detecting the molecules remaining in
88 the solid phase by means of an infrared spectrometer (Sandford and Alla-
89 mandola (1993)), measuring the column density, but when phase changes are
90 involved, this could lead to experimental errors, ii) detection most of the des-
91 orbing molecules by using a mass spectrometer, in a typical temperature pro-
92 grammed desorption (TPD) experiments, carried out under ultra high vacuum
93 conditions (Muñoz Caro et al. (2010)), or iii) measuring directly the desorbing
94 molecules by using the analysis of the signal of a quartz crystal microbalance
95 (QCMB) during desorption (Luna et al. (2009)).

96 In a previous work (Luna et al. (2009)) we have developed a method to cal-
97 culate the desorption energy based on the analysis of the signal variation of
98 a QCMB under high vacuum conditions. Using this result, it is possible to
99 design a procedure to calculate A_0 (frequency factor) in the Polanyi-Wigner
100 equation for zeroth order desorption processes. This parameter is suitable to
101 determine desorption rate necessary to study desorption process of molecules
102 present in different environments.

103 To explain the method to obtain A_0 , in section 2 the experimental setup is
104 described, in section 3 the experimental procedure and results are presented,
105 in section 4 results are discussed and finally, conclusions are exposed in section
106 5.

107 2 Experimental setup.

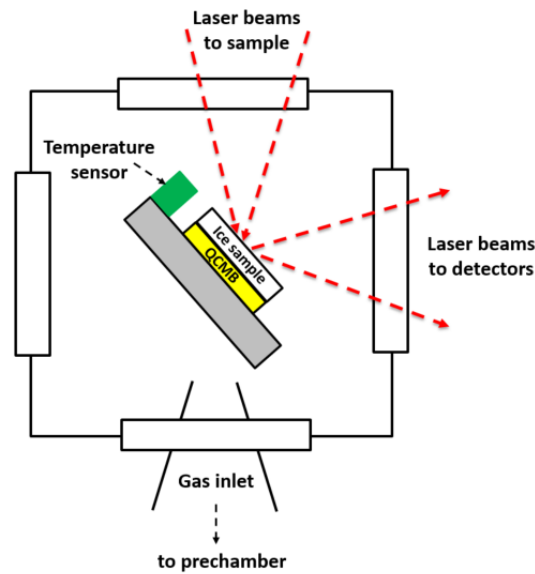


Fig. 1. Disposition of the laser beams and location of the temperature sensor, QCMB and sample.

108 Experiments are carried out in a system working under high vacuum (HV)
109 conditions. The main components are a QCMB (1.0 cm^2 of surface) and a
110 temperature sensor controlled externally (Fig. 1).

111 The pressure of the experiment (10^{-7} mbar) is obtained by assembling a couple
112 of turbomolecular pumps backed by their corresponding rotary pump and the
113 help of a closed-cycle He cryostat acting as a cryopump. Gas under study
114 is previously charged in a prechamber. To control the constant flow of the

115 molecules entering the chamber, two parameters are regulated: the pressure
116 in the prechamber (measured with a Ceravac CTR 90, Leybold Vacuum) and
117 the degree of aperture of a needle valve (Leybold D50968).

118 The edge of the cryostat is in thermal contact with the QCM (Q-Sense gold
119 coated quartz, 5 MHz). The temperature of the sample (deposited onto the
120 QCM) is governed by the Intelligent Temperature Controller ITC 503S (Ox-
121 ford Instruments), using a silicon diode sensor (Scientific Instruments) located
122 just beside the quartz and a heating resistor, allows the temperature to vary
123 between 13.0 and 300.0 ± 0.1 K, by means a resistor. This controller allows to
124 carry out several kind of procedures: i) fixing a constant temperature in the
125 QCM, ii) obtaining a constant ramp of warming up or even iii) obtaining
126 increasing temperatures at selected steps. To control the thickness during the
127 growth, interferometric patterns are obtained by means a double He-Ne laser
128 (632.8 nm) system.

129 The following chemical has been used in this research: C_2H_6 – 99.99 (Praxair).

130 **3 Experimental procedure and results**

131 The procedure carried out to calculate the frequency factor in the Polanyi-
132 Wigner equation and to study how temperature influences this parameter, is
133 performed in two steps based in different types of experiments.

135 In a first step, a desorption at a constant rate of warming up is performed. The
136 raw signal recorded during deposition and desorption for one experiment of
137 C_2H_6 is shown in Fig. 2, where QCM frequency signal versus time is plotted.
138 Two parts are clearly differentiated in this plot: a first interval (from 4200 to
139 5400 s), where the deposit is performed. The starting point of the deposition
140 is around 4500 s, where the frequency signal starts to decrease with a constant
141 slope due to a constant rate of mass deposition onto the QCM over the sample
142 holder (40 K). The Sauerbrey equation $\Delta F = -S \cdot \Delta m$ shows the relationship
143 between the QCM frequency variation ΔF and the variation of the deposited
144 mass Δm through the constant S (65 Hz/ μ g) of our system. When a thickness
145 around 1.0 micron is achieved (measured with the interference fringes obtained
146 by the laser beam), deposition is stopped. The second part of the experiment
147 corresponds to a desorption process starting around 7000 s in Fig. 2 (right),
148 using a heating ramp of 1 K min^{-1} , as it is widely used by other authors for
149 similar processes. From the signal recorded in the interval ranging from 7000
150 to 8000 s, it is possible to calculate the desorption energy, but as a previous
151 step it is necessary to improve the original signal obtained taking into account
152 two effects during the experiment: influence of the temperature in the QCM
153 frequency signal and the presence of contaminants (mainly water) in the signal.
154 The detailed procedure to remove these effects is explained in detail in (Luna
155 et al. (2009)).

156 Once the signal is cleaned, desorption energy is calculated using the Polanyi-
157 Wigner equation.

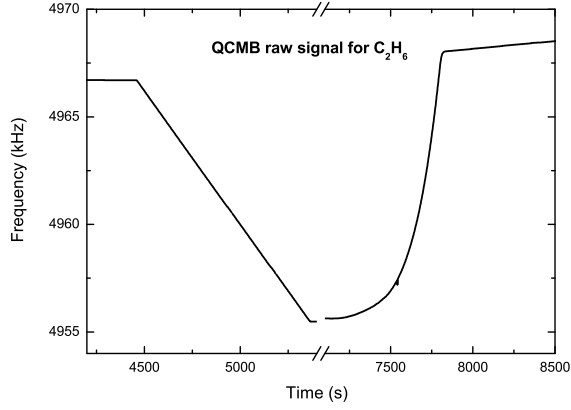


Fig. 2. Raw QCM signal during deposition at constant temperature (left) and desorption at a constant ramp of temperature 1 K min^{-1} (right) for C_2H_6 .

$$-\frac{dN}{dt} = A_i \cdot N^i \cdot \exp\left(-\frac{E_{des}}{R \cdot T}\right) \quad (2)$$

Taking $-dN/dt$ as the desorption rate (r_{des}) of molecules from the QCM, and assuming a zeroth order desorption process for our experiments, we obtain a more suitable expression:

$$r_{des} = A_0 \cdot \exp\left(-\frac{E_{des}}{R \cdot T}\right) \quad (3)$$

where r_{des} and A_0 are in $\text{molecule cm}^{-2}\text{s}^{-1}$. Experimentally, r_{des} has been obtained by applying the derivative of the frequency versus time for the signal presented in Fig. 2. The corresponding derived plot is shown in Fig. 3, where r_{des} is represented against temperature. From the peak obtained in this plot, we directly assign the desorption temperature (under our experimental conditions) corresponding to the molecule studied (82 K for C_2H_6) and from the profile of the curve we confirm the assumption of a zeroth order desorption (Luna et al. (2009)) typical of a multilayer desorption.

Now, taking the natural logarithm from Eq. (3), a linear expression is reached:

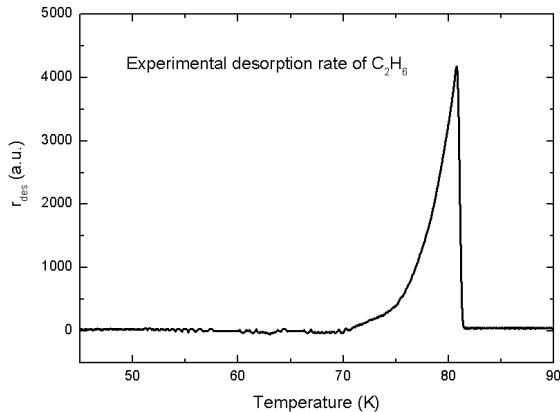


Fig. 3. Desorption rate for C_2H_6 .

$$172 \quad \ln(r_{des}) = \ln(A_0) - \frac{E_{des}}{R} \cdot \frac{1}{T} \quad (4)$$

173 Therefore, a plot of $\ln(r_{des})$ versus $1/T$ leads to a straight line whose slope
 174 is $-E_{des}/R$. Fig. 4 represents this final step. From the slope, E_{des} is derived.
 175 In Table 2 we present the values obtained for the fit shown in Fig. 4. The
 176 desorption energy calculated is $E_{des} = 19.3 \text{ kJ mol}^{-1}$. In Table 3 we compare
 177 our results with other values obtained previously in the literature. As can be
 178 observed, there is a good agreement among our result and the scarce earlier
 179 ones reported.

180 Despite it is assumed by some authors that A_0 could be reached from the in-
 181 tercept of this linear fit, this value is not appropriated. The main reason is the
 182 impossibility to assign A_0 to a specific temperature due to the continuous tem-
 183 perature change during the experiment, and additionally, the intercept could
 184 be affected by some systematical errors not affecting to the slope of the signal
 185 recorded. Therefore it is necessary to obtain this parameter in a different way
 186 which implies to perform several desorption experiments at different constant
 187 temperatures to obtain the factor frequency for every temperature.

188 Therefore this first step is suitable to obtain E_{des} , but it is not appropriate

Table 2

Parameters obtained for the linear fit to calculate desorption energy (plot of Fig. 4).

Parameter	Value	Standard Error
Slope = $(-E_{des}/R)$	-2321	7
Intercept	37.66	0.09
Regression coefficient	0.998	

189 to derive how temperature influences A_0 . Then, a second procedure must be
 190 implemented to study A_0 as a function of temperature, where E_{des} calculated
 191 in previous step, is a necessary parameter.

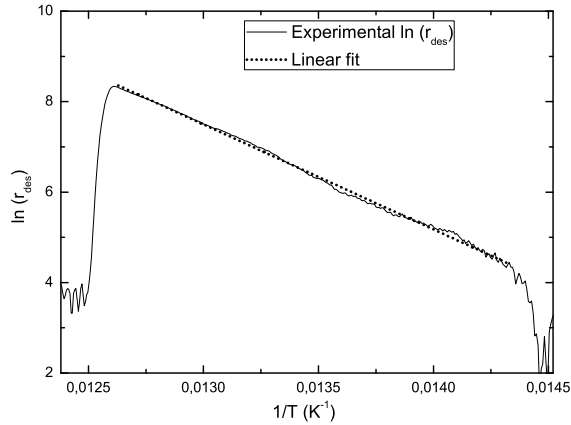


Fig. 4. The $\ln(r_{des})$ versus $1/T$ (straight line) and linear fit (dotted line) for C_2H_6 .

192 *3.2 Frequency factor A_0 versus temperature*

193 To study how temperature influences the frequency factor A_0 , an additional
 194 set of experiments has been implemented, each one is carried out at a selected
 195 constant temperature. From Eq. (3), if temperature is constant, a constant des-
 196 orption rate is obtained. In terms of QCMB frequency signal, it corresponds

Table 3

C₂H₆ desorption energy comparison with other previous results from the literature.

This work		NIST	
T _{des}	E _{des}	T _{interval}	E _{des}
(K)	(kJ mol ⁻¹)	(K)	(kJ mol ⁻¹)
82	19.3 ± 0.5	90	20.5, a
		80-90	22.5, b
a: Bondi (1963)			
b: Regnier (1972)			

Table 4

Experimental values obtained for desorption of C₂H₆ at different constant temperatures. Column 1 represents the experimental temperature, column 2 is the desorption rate calculated, and column 3 shows the A₀ obtained for each temperature using the Polanyi-wigner equation.

Temp.	r _{des} = -ΔN/Δt	A ₀
K	10 ¹⁵ molecule cm ⁻² s ⁻¹	10 ²⁹ molecule cm ⁻² s ⁻¹
68	0.54	3.6
70	1.7	4.3
72	5.2	5.2
74	14	5.7

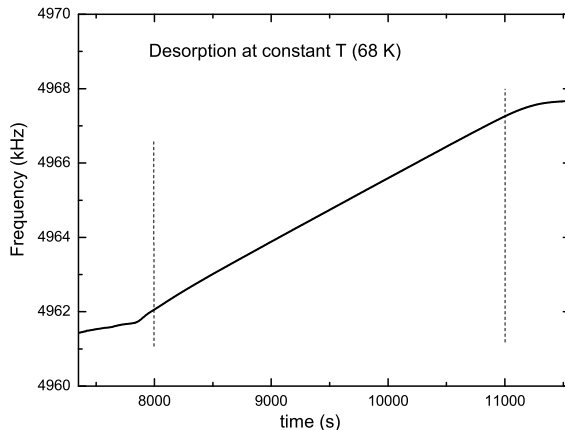


Fig. 5. Desorption experiment at a constant temperature of 68 K for C_2H_6 .

197 to a straight line of constant positive slope when frequency is represented
 198 versus time, as can be seen in Fig. 5 (interval between two vertical dotted
 199 lines), where desorption has been carried out at 68 K. The set of tempera-
 200 tures used to perform these experiments have been meticulously selected as
 201 follows: to obtain a reasonable desorption rate, temperature must be close to
 202 82 K (for C_2H_6 desorption experiments) in order to be measurable during a
 203 typical experiment. But, for temperature too close to 82 K no many experi-
 204 mental points would be obtained during the short time that the experiment at
 205 these temperatures takes place and then, experimental errors would be larger.
 206 Additionally, for temperatures too lower, negligible desorption rate would be
 207 obtained, and experiments could even last several days. Therefore taking in
 208 consideration the previous statements, our selected experimental desorption
 209 temperatures have been the following ones: 68, 70, 72 and 74 K (Fig. 3 shows
 210 their corresponding desorption rate).

211 From the analysis of the signal obtained for each temperature and assuming
 212 a constant E_{des} with temperature, A_0 is derived for the corresponding exper-
 213 iment, taking the antilogarithm from the following expression:

214
$$\ln(A_0) = \ln(r_{des}) + \frac{E_{des}}{R \cdot T} \quad (5)$$

215 obtaining

216
$$A_0 = \exp\left(\ln(r_{des}) + \frac{E_{des}}{R \cdot T}\right) \quad (6)$$

217 where r_{des} has been calculated experimentally as

218
$$r_{des} = \frac{-\Delta N}{\Delta t} = \frac{-\Delta F}{\Delta t} \cdot \frac{\Delta m}{\Delta F} \cdot \frac{1}{M_r} \cdot N_A \quad (7)$$

219 where t is the experimental time, $\frac{\Delta m}{\Delta F}$ is S^{-1} (S is the Sauerbrey constant
220 mentioned above) and M_r is the molar mass. Finally

221
$$r_{des} = \frac{-(F_2 - F_1)}{t_2 - t_1} \cdot S^{-1} \cdot \frac{1}{M_r} \cdot N_A \quad (8)$$

222 where F_1 , F_2 , t_1 and t_2 are the corresponding values for frequency and time at
223 the starting and ending points respectively of the straight line obtained from
224 the QCM signal during desorption at constant temperature (see Fig. 5 for the
225 case of 68 K desorption). Table 4 shows the experimental values obtained for
226 this analysis. Column 2 represents the desorption rate experimentally mea-
227 sured and in column 3 the value of A_0 calculated for each temperature is
228 presented. Our values are in the range of the values reported by other authors
229 (see Table 1).

230 The linear fit of A_0 versus temperature (see Table 5) provides the following
231 expression $A_0 = 3.6 \cdot 10^{28} \cdot T - 2.1 \cdot 10^{30} (\text{molecule cm}^{-2} \text{s}^{-1})$ for C_2H_6 under
232 our experimental conditions.

Table 5

Parameters obtained for the linear fit to obtain $A_0 = f(T)$.

Parameter	Value	Standard Error
Slope	$3.6 \cdot 10^{28}$	$0.2 \cdot 10^{28}$
Intercept	$-2.1 \cdot 10^{30}$	$0.1 \cdot 10^{30}$
Regression coefficient	0.994	

Table 6

Estimated A_0 and r_{des} at different temperatures and desorption time for a deposit with a column density of $1.0 \cdot 10^{18} \text{ molecules cm}^{-2}$.

Temperature	A_0	$r_{des} = -\Delta N/\Delta t$	Desorption time
K	$10^{28} \text{ molecule cm}^{-2}\text{s}^{-1}$	$10^{16} \text{ molecule cm}^{-2}\text{s}^{-1}$	10^8 s
60	6.0	0.000097	10
65	24	0.0076	0.13
70	42	0.17	0.0059
75	60	2.2	0.00045
80	78	20	0.000050

233 4 Discussion

234 Among other applications, the Polanyi-Wigner equation is widely used to cal-
 235 culate the desorption energy for a substance from its solid phase or from a
 236 surface where the molecule is adsorbed. For this case, in the literature, a negli-
 237 gible variation with temperature for the frequency factor A_i has been assumed.

Table 7

Desorption rate calculated for 70 K using different values for A_0 .

Desorption Temperature K	Temperature used to calculate A_0 K	A_0 10^{28} molecule $\text{cm}^{-2}\text{s}^{-1}$	$r_{des} = -\Delta N/\Delta t$ 10^{14} molecule $\text{cm}^{-2}\text{s}^{-1}$
70	60	6.0	2.4
70	65	24	9.7
70	70	42	17
70	75	60	24
70	80	78	32

238 Then it has been taken as a constant parameter when the Polanyi-Wigner
 239 equation is used for calculation purposes, despite activated state theory de-
 240 clares how temperature influences A_i . In the present work we have experimen-
 241 tally determined how temperature influences this parameter for the case of
 242 C_2H_6 desorption.

243 We have selected the temperatures 68, 70, 72 and 74 K to obtain A_0 from
 244 desorption experiments at these constant temperatures. As a result, we have
 245 obtained an expression for the frequency factor $A_0 = 3.6 \cdot 10^{28} \cdot T - 2.1 \cdot$
 246 10^{30} (molecule $\text{cm}^{-2} \text{s}^{-1}$) for the interval 68 to 74 K in which a reasonable
 247 desorption rate (for laboratory experiments purposes) occurs. In Table 4 we
 248 show the values of A_0 for the zeroth order desorption process implied when
 249 a multilayer desorption occurs. An increase around 50% is obtained when
 250 temperature increases from 68 to 74 K.

251 Using the expression obtained, and assuming that it can be extrapolated to the
 252 interval 60 – 80 K (being 82 K the sublimation temperature), we can calculate
 253 the desorption rate for temperatures within this interval (see Table 6) and the
 254 interval of time that a zeroth order desorption for a deposit with a column
 255 density of for example $1.0 \cdot 10^{18} \text{ molecule cm}^{-2}$ would take. There is a difference
 256 of six orders of magnitude from desorption rate at 60 K and desorption rate
 257 at 80 K. Therefore, for this molecule, desorption at temperatures lower than
 258 60 K could be considered as negligible for this kind of experiments.

259 To estimate the influence of A_0 for a typical desorption, we have calculated
 260 the desorption rate at constant temperature ($T = 70 \text{ K}$) using values of A_0
 261 associated to temperatures ranging from 60 to 80 K (see Table 7). As can
 262 be observed, r_{des} increases as the temperature used to calculate A_0 increases.
 263 Quotient between maximum and minimum values is equal to 13, which seems
 264 relevant to estimate the interval of time that a desorption process will last in a
 265 certain environment in order to design this kind of experiments, for theoretical
 266 calculations, etc.

267 Additionally, to estimate how the assumption of the constancy of A_0 affects to
 268 the value of E_{des} , we have calculated E_{des} (see Table 8) for the temperatures
 269 at which we have performed the desorption experiments (68, 70, 72 and 74 K)
 270 assuming for all of them the same value of $A_0 = 4.2 \cdot 10^{29} \text{ molecule cm}^{-2} \text{ s}^{-1}$
 271 (corresponding to 70 K), using the expression

$$272 \quad E_{des} = R \cdot T (\ln(A_0) - \ln(\Delta N / \Delta t))$$

273 where $\Delta N / \Delta t$ is the experimental value obtained for each temperature. As
 274 can be seen, desorption energy decreases as temperature increases. A differ-

Table 8

Desorption rate E_{des} calculation at different temperatures, assuming a constant value for $A_0 = 4.20 \cdot 10^{29}$ molecules $\text{cm}^{-2} \text{s}^{-1}$.

Temperature	$r_{des} = -\Delta N/\Delta t$	E_{des}
K	10^{15} molecule $\text{cm}^{-2}\text{s}^{-1}$	kJ mol^{-1}
68	0.54	19.4
70	1.7	19.3
72	6.0	19.1
74	14	19.1

275 ence around 1% is obtained for an increase of 6 K. this difference is within
 276 the error bars. Additionally, since desorption experiments at constant temper-
 277 ature are most likely performed within this interval of temperatures (for the
 278 reasons exposed above), for this molecule, the assumption of considering A_0
 279 as a constant for the Polanyi-Wigner equation does not affect significantly the
 280 result.

281 5 Conclusions

282 Frequency factor A_0 , is a parameter of the Polanyi-Wigner equation which is
 283 necessary to calculate desorption rates for any species under suitable condi-
 284 tions to desorb. In the literature, variation with temperature for A_0 has been
 285 usually neglected when this parameter has been used to calculate E_{des} from
 286 the Polanyi-Wigner equation. This latter magnitude has been calculated as-
 287 suming the constancy of A_0 in a desorption process where the temperature

288 varies continuously, obtaining an interval of values ranging from 10^{27} to 10^{32}
289 for zeroth order processes or it is assumed as $A_1 \cdot N$, taking $A_1 = 10^{12} \text{ s}^{-1}$ and
290 $N = 10^{15} \text{ molecules cm}^{-2}$.

291 In this paper we show a procedure to experimentally calculate for the first time
292 the frequency factor, and to study how temperature influences this parameter
293 for the Polanyi-Wigner equation. For this purpose, the analysis of the QCMB
294 signal for a zeroth order desorption has been used.

295 To study whether the effect of the temperature is relevant on the frequency
296 factor A_0 , we have used two kind of experiments based on zeroth order des-
297 orption as assumed for the case of multilayer deposits. From the first one,
298 based on a desorption at a constant ramp of temperature, we have obtained
299 desorption energy E_{des} for C_2H_6 . This value has been compared with those
300 previously reported in the literature and a good agreement is found, despite
301 our experiments are performed at lower temperatures because of desorption
302 pressure conditions. From the second set of experiments, based on desorption
303 experiments at a constant temperature, we have studied the variation of A_0
304 against temperature. As a result, we find a linear variation for the interval 68
305 to 74 K, $A_0 = 3.6 \cdot 10^{28}T - 2.1 \cdot 10^{30}$, which implies an increase of A_0 around
306 50% within this interval. The results obtained are in the interval of the previ-
307 ous results reported obtained by other methods. Therefore, our results results
308 must be taken into account to calculate the desorption rate of a typical exper-
309 iment in the laboratory or in an environment where a similar temperature is
310 present as could be the case of astrophysical scenarios or cryogenic samples.

311 The influence of A_0 on the calculation of E_{des} has also been explored, but for
312 this case no significant variation is detected. Then, as a first approach it is

313 justified to assume a constant value of A_0 to calculate desorption energy.

314 Additionally, once the frequency factor A_0 is obtained for a specific molecule
315 (for zeroth order desorption experiments), it can be used to estimate the cov-
316 erage N for other order processes from the desorption rate measured with the
317 QCMB.

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