

A STUDY OF RADON ADSORPTION ON ACTIVATED CARBON AS A FUNCTION OF TEMPERATURE

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ABSTRACT

The adsorption of radon-222 on activated carbon varies with temperature and the presence of other gases. We have developed a simple physical model that accounts for the variation as a function of temperature over the range of 0 to 200 degrees C.

INTRODUCTION

A number of radon measurement and remediation techniques employ activated carbon adsorption, which has well known sensitivities to temperature and humidity. Successful design and analysis of adsorption systems requires an adequate understanding of these sensitivities.

Several papers on radon sampling devices have addressed in some detail the issue of temperature effect. Prichard and Marien (1985) developed an excellent model of the passive integrating radon sampling device, including an empirical expression for the effect of temperature on adsorption from -10 to 40 degrees C. Pojer et al. (1990) suggested a temperature effect based on the Arrhenius expression, with an activation energy in the range of 24 to 37 kJ/mol.

THEORY

Radon, an inert gas, adsorbs onto surfaces by means of physical non-chemical interaction. Atkins (1986) describes the process of physical adsorption, or "physisorption", as a long-range but weak interaction of a molecule with a surface. The energy released in the adsorption of a molecule is known as the enthalpy of adsorption, and is usually comparable in magnitude to the enthalpy of condensation for that molecule, which is around 17 kJ/mol for radon. When a radon molecule strikes a surface it may either bounce off the surface, or if it strikes an "adsorption site", it may dissipate enough energy to become physically adsorbed to the surface.

As molecules adsorb onto a particular surface, adsorption sites can become filled, and so become unavailable for further adsorption. In our experiments, the number of available adsorption sites always greatly exceeds the number of radon molecules present, so we do not expect the filling of sites with radon molecules to lead to a significantly reduced adsorption probability for other radon molecules. On the other hand, more plentiful gaseous molecules such as water vapor can definitely exclude radon from adsorption sites, so we have carefully controlled the presence of water vapor in our experiments.

A physically adsorbed molecule will eventually desorb from the surface. Due to thermal agitation, the adsorbed molecule "vibrates" within the adsorption site, and with every vibration there is a chance that the weakly bound molecule will leave the site. The probability that desorption will occur within a certain time period greatly increases as temperature rises. The Arrhenius rate equation, an exponential function involving activation energy and temperature, characterizes this process.

The interplay of adsorption and desorption processes determines an equilibrium condition whereby the amount of material being adsorbed compensates the amount of material being desorbed and there is no net change over time. This equilibrium condition is the subject of this study.

MATERIALS AND METHODS

The apparatus (fig. 1) is a closed system of fixed volume composed of a sample cell, a radon gas monitor, several coils of copper tubing, and a drying tube. The sample cell, constructed of copper and brass pipe and fittings, can contain up to 20 grams of activated charcoal. A NITON RAD7 radon gas monitor serves to circulate air through the sample and measure the air radon gas concentration. The adsorbent sample cell sits inside a temperature controlled environmental chamber, while the radon gas monitor and drying tube stay outside the chamber at room temperature. The drying tube contains 30 grams of calcium sulfate desiccant to maintain humidity at very low concentrations. The coils of copper tubing serve as heat exchangers to bring the air stream up to the chamber temperature before it passes through the charcoal, and to bring the air stream down to room temperature before it passes through the desiccant and radon monitor. A personal computer records both radon concentration from the radon gas monitor and chamber temperature from a thermocouple.

In a typical experimental run we would introduce a spike of radon gas to the system, allow the system to equilibrate, then begin ramping the chamber temperature slowly up to 200 degrees C. Once the temperature reaches 200 degrees C, we would hold that temperature for a short period, then begin to ramp the temperature slowly downward to 20 degrees C. After holding the temperature for a short time, we would ramp the temperature upward to repeat the entire cycle. All temperature changes are made very slowly (0.2 degrees per minute or less) to ensure that the adsorbent and gas stay as close to the equilibrium condition as possible.

MATHEMATICAL MODEL

The rate that radon molecules reach the adsorbent surface and adsorb to it is given by

$$\text{Rate(on)} = C_a' * \text{sqrt}(kT / m) * A * S$$

where C_a' is the concentration of radon molecules in the air adjacent to the surface, A is the area of the surface, S is the "sticking probability" with geometric adjustment, and $\text{sqrt}(kT / m)$ is the average velocity of gas molecules normal to the adsorbent surface where k is the Boltzmann constant (8.314 J/mol-K), T is absolute temperature, and m is the mass of the molecule.

The rate that radon molecules desorb from the surface is given by the Arrhenius-style rate function

$$\text{Rate(off)} = N_c * F(T) * \exp(-E / kT)$$

where N_c is the number of radon molecules adsorbed on the surface of the carbon, $F(T)$ is the frequency of the adsorbed molecule's vibrations, and $\exp(-E / kT)$ is the Boltzmann factor giving the probability that a particular vibration of the molecule will release it from the adsorption site. E designates the activation energy for desorption, which is closely related to the adsorption enthalpy. We suppose that the vibration frequency is a function of temperature, perhaps proportional to the molecular velocity. If this is the case then

$$F(T) = F_0 * \text{sqrt}(T / T_0)$$

where F_0 is the vibration frequency at a particular base temperature T_0 . Substituting this expression into the above expression for Rate(off) , we have

$$\text{Rate(off)} = N_c * F_0 * \text{sqrt}(T / T_0) * \exp(-E / kT).$$

The equilibrium condition requires that Rate(on) equals Rate(off) . Equating these, we can eliminate a factor of $\text{sqrt}(T)$ and algebraically rearrange to get

$$N_c = (S * A * \text{sqrt}(kT_0 / m) / F_0) * C_a' * \exp(E / kT).$$

In this equation, the constants A, S, and F0 are properties of the adsorbent, but we do not know these constants to any degree of confidence. We define a geometric constant G to lump these constants together. If

$$G = S * A * \sqrt{kT_0 / m} / F_0,$$

then

$$N_c = G * C_a' * \exp(E / kT).$$

The number of radon molecules in the air loop, N_a , divided by the volume, V_a , gives the radon concentration in the air loop, C_a , which is the quantity we measure. C_a is not exactly the same as C_a' , since C_a' is the concentration of the air at the surface of the adsorbent, which is at a different temperature from the rest of the air loop. Since at a constant pressure the volume of a given quantity of air increases with rising temperature, the radon concentrations of warm air and cool air will be in inverse proportion to their absolute temperatures, so

$$C_a' = C_a * (T_0 / T)$$

and

$$N_c = G * C_a * (T_0 / T) * \exp(E / kT).$$

We define V_c as an "equivalent volume" of air for the adsorbent such that if the adsorbent is in equilibrium with air having a radon concentration of C_a , then the adsorbent behaves as a volume of air V_c at the same radon concentration C_a . So, clearly, $N_c = C_a * V_c$ and

$$V_c = G * (T_0 / T) * \exp(E / kT)$$

by comparison to the above equation. Note that if the adsorbent and air loop had been at the same temperature, the function for V_c would not have required the factor of (T_0 / T) . If we define V_0 as the equivalent volume V_c at the base temperature T_0 , then

$$V_0 = G * \exp(E / kT_0)$$

and by substitution

$$V_c = V_0 * (T_0 / T) * \exp((E / kT) - (E / kT_0)).$$

After correcting for radioactive decay, we can assume that the total amount of radon is a constant. That is,

$$N_c + N_a = N_t$$

where N_t is the constant total amount of radon in the system. The equivalent volume of the complete system, with air loop and adsorbent, at C_a is $V_a + V_c$, so our system equation is

$$C_a = N_t / (V_a + V_c)$$

and by substitution of V_c the system equation becomes

$$C_a = N_t / (V_a + V_0 * (T_0 / T) * \exp((E / kT) - (E / kT_0)))$$

where N_t , V_a , V_0 , T_0 , E , and k are constants within the experiment, and C_a varies as a function of T . Actually, we can improve the model by allowing V_a to vary slightly with temperature since a fraction of the air loop is contained within the environmental chamber and is subject to gas expansion as the chamber heats up. In this improved model

$$V_a = V_{a1} + V_{a2} * (T_0 / T)$$

where V_{a1} is the volume of air kept at room temperature and V_{a2} is the volume of the air loop subject to gas expansion and contraction.

EXPERIMENT PARAMETERS

We repeated the experiment several times, making a number of refinements along the way. In the final configuration the experiment used these parameters:

Adsorbent:	Activated carbon United Desiccants (Belen, NM)
Dry mass:	1.000 grams
Desiccant:	Indicating Drierite (97% CaSO ₄), 10-20 mesh W.A. Hammond Drierite Co. (Xenia, OH)
Dry mass:	30 grams
Air loop volume total (Va):	1.135 liter
Air loop at room temp (Va1):	0.960 liter
Air loop in chamber (Va2):	0.175 liter
Air flow rate (nominal):	1.0 liter/minute
Average room temperature (T0):	27 deg C (300 deg K)
Chamber temperature range:	20 to 200 deg C
Temperature ramp up rate:	0.2 deg/minute
Temperature ramp down rate:	0.2 deg/minute
Hold time at end of range:	3 hours
Number of complete cycles:	2

DATA ADJUSTMENT

After adjusting the radon concentration data for radon's natural radioactive decay (3.825 day half-life), we discovered that repeat cycles showed slowly diminishing radon measurements. After becoming satisfied that there were no significant changes to the adsorbent or the instrumentation, we determined that the most likely reason for the lowered radon measurements was a small leak in the air loop. An adjustment to the data to account for leakage from the system produced excellent correlation of the radon concentration from cycle to cycle.

FITTED PARAMETERS

Since N_t , V_0 , and E were not known at the time of the experiment, we used a 3 parameter minimum chi-squared fit to match the experimental data (fig. 2) to the system equation derived above. Although the fit gave an excellent match to the data, we were concerned about the uncertainties involved in fitting 3 parameters. An independent measurement of the equivalent volume (V_c) of the same 1.000 gram adsorbent sample at 25.6 deg C gave a result of 4.53 ± 0.12 liters. Interestingly, this result puts the sample among the highest performing of 20 activated carbon based radon adsorbents tested by Scarpitta (1992).

MEASUREMENT UNCERTAINTIES

Several aspects of the experiment as performed lead to uncertainty in the results. Some sources of uncertainty are difficult to quantify, so we suggest caution in interpreting the given error figures.

The radon concentration measurements have a statistical error inherent to the counting of radioactive decay events. But the overall error was more than double what counting statistics would indicate.

We suspect that the small air leak and its correction discussed above could introduce a degree of error to the radon data. The temperature measurement is another source of error due to the imprecision of the apparatus we used. This part of the experiment is a prime candidate for improvement in further investigations.

Another significant source of error is the nature of the 3 parameter fit used to match the data to the model. An effort to reduce the number of fit parameters by separate measurement of Nt and/or V0 could lead to an improved accuracy of the result for E.

In order to understand the effect of correlated error among the fit parameters, we plotted chi-square contours for pairs of the parameters. The chi-square contours show significant correlation among the parameters such that the range of value bounded by a contour is much larger than would be indicated by a single parameter plot. The uncertainties given with the results reflect the range of value bounded by the minimum-chi-square- plus-one contour.

Other sources of error include deviations of the physical system from the very simple model presented here. For example, the model presumes that the vibrational frequency of the adsorbed molecule is proportional to the square root of absolute temperature. The model also presumes that all adsorption sites have identical activation energies when in fact there may exist several different types of adsorption sites, each type of site having a different activation energy.

RESULTS

Parameters for the fitted curve shown in figure 2 are:

$$\begin{aligned} Nt &= 4380 \pm 390 \text{ (pCi)} \\ V0 &= 4.64 \pm 0.33 \text{ (liters)} \\ E &= 31.5 \pm 2.1 \text{ (kJ/mol)} \end{aligned}$$

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- Pojer, P.M., et al. Performance of a Diffusion Barrier Charcoal Adsorption ²²²Rn Monitor Under Conditions of Varying Humidity and Temperature. *Health Physics* 58(1):13-19; 1990.
- Prichard, H.M., and K. Marien. A Passive Diffusion ²²²Rn Sampler Based on Activated Carbon Adsorption. *Health Physics* 48(6):797-803; 1985.
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Figure 1: Apparatus for determining radon adsorption as a function of temperature.

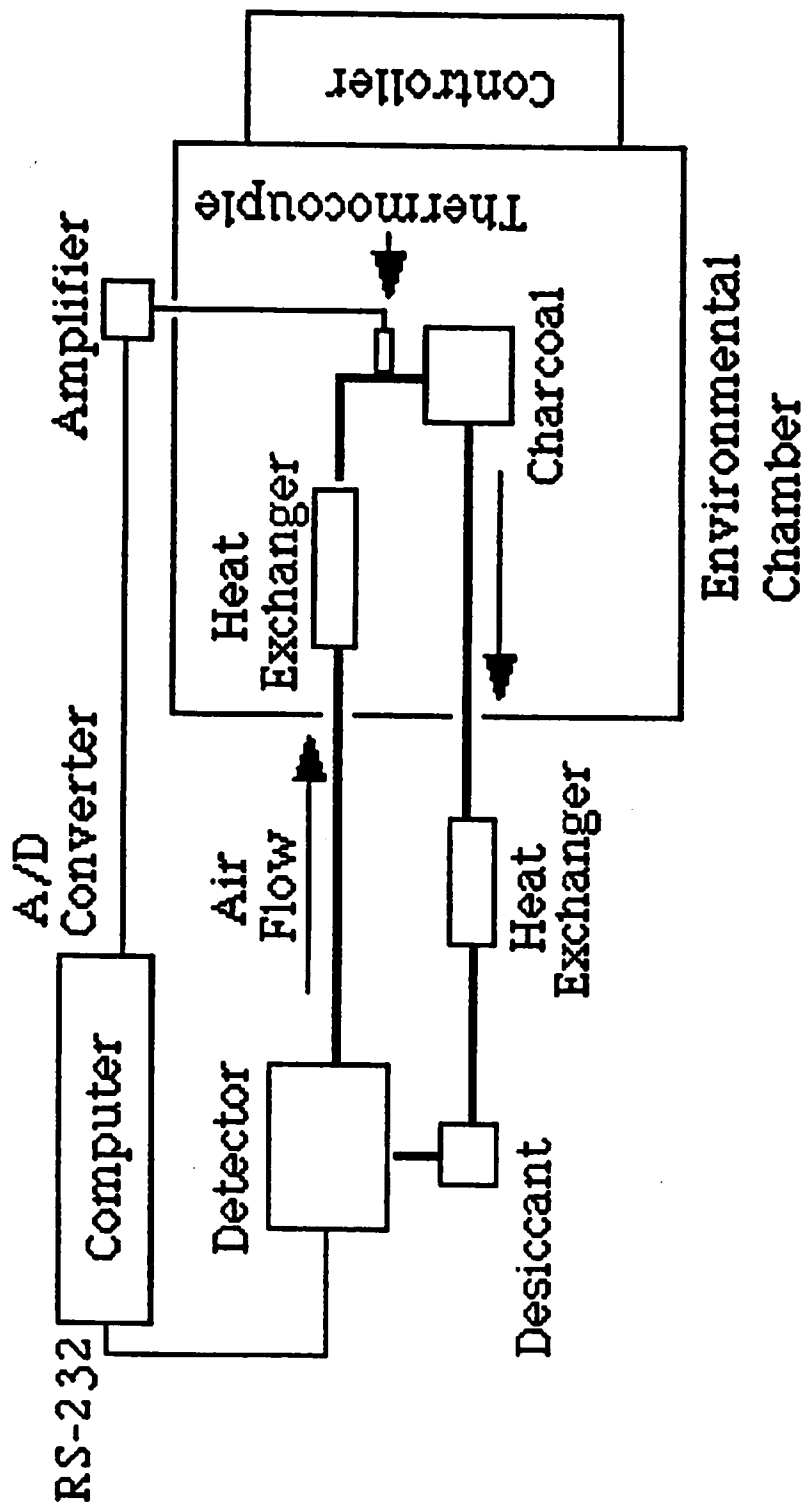


Figure 2: Three parameter fit to data from radon adsorption as a function of temperature.

