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**Noble Gas Separation by Adsorptive Phenomena
in Mass Spectrometry**

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For precise measurements of noble gases with a mass spectrometer, we need to separate each noble gas by adsorptive phenomena at low temperatures. We made adsorptive experiments for Ar, Kr, and Xe using a cold trap containing a sintered stainless steel filter element. In this paper, we applied a simple model to our experimental observations in order to better understand the adsorptive phenomena on the adsorbent, and obtained the conditions for more efficient separation of individual noble gas. The results suggest that the adsorption curves shift to a higher temperature when we release gas in a smaller volume of the extraction line. This temperature shift is larger for a noble gas with a higher mass. Therefore, small volume of preparation line is suitable for the clear separation of noble gases. It is also shown that the adsorption curve depends on the pressure of gases when the total number of gas atoms in the line is not negligible compared to the maximum number of atoms being adsorbed.

1. Introduction

In the precise measurements of noble gases with a mass spectrometer, we generally separate each noble gas by adsorption on the surfaces of a sintered stainless steel element and/or activated charcoal at low temperatures.

Activated charcoal was first used as adsorbent for noble gas separation.¹⁾ At first, the temperature of charcoal was preserved at liquid nitrogen temperature (77 K), which could trap essentially all the heavy noble gases (Ar, Kr, and Xe). Neon and helium are not adsorbed on the charcoal to any appreciable extent at 77 K. All or part of the unsorbed gases are transferred to a mass spectrometer for the analysis of helium and neon. Next, the temperature of the charcoal was controlled by attaching it to a small heater which is separated from a liquid nitrogen reservoir by a thermal resistance. By adjusting the power in the heater, the temperature of the charcoal can be electrically regulated at any desired value of outgassing conditions of the heavy noble gases. Reynolds *et al.* (1978)²⁾ reported a charcoal trap whose temperature could be controlled down to about 20 K using a helium expansion refrigerator. At this temperature, both helium and neon are completely adsorbed on activated charcoal, making it possible to separate these light noble gases in the same manner as that used for the heavier ones.³⁾ Recently, many researchers have started to use a sintered stainless steel element as an adsorbent in the gas preparation line connected to the mass spectrometer⁵⁾ because of its cleanness which is very suitable for the noble gas measurement under ultra-high vacuum.

Until now, adsorptive experiments for noble gases were made only to determine the optimum separation temperatures among them. We made adsorption experiments for Ar, Kr, and Xe using a new preparation line for noble gas measurements in our laboratory. In this report, we applied a theoretical model to our experiments in order to understand the adsorptive phenomena of such element in the noble gas preparation line and to obtain the more efficient separation of noble gases for their precise measurement.

2. Experiments of Adsorptive Phenomena and Results

Our vacuum line for noble gas preparation consists of two purification lines each of which contains a Ti-Zr getter and a cold trap (Fig. 1) and is directly connected to the mass spectrometer. A sintered stainless steel element (SS-8F-K4-05, Nupro Co.) with the particle size of $0.5\ \mu\text{m}$ was used as an adsorbent of noble gases for the second cold trap (CT-2). The cold trap was cooled with liquid nitrogen and the temperature was controlled at our desired value (from 77 K to ~ 273 K) using a small heater placed around the cold trap. The temperature was monitored by an almel-chromel thermocouple wire attaching between the heater and the cold trap. Temperature regulation is ± 1 K by means of a temperature controller (E5CX, OMRON Co.) which switches on/off the current as the monitored temperature is below/above the desired value. Pipetted air (containing $6.7 \times 10^{-7}\ \text{cm}^3$ STP of ^{40}Ar) was purified with two Ti-Zr getters at about 700°C for 15 min. and expanded into the analyzing tube of the mass spectrometer after trapping most gases on the CT-2 at the temperature of the liquid nitrogen temperature (77 K). The temperature of CT-2 was increased with intervals of a few K from the liquid nitrogen temperature and maintained at each temperature for more than a few min. to attain temperature equilibrium. The quantities of the released gases were measured with the mass spectrometer at each temperature step. In this time scale we need not to consider the loss/gain of gases in the mass spectrometer. Figure 2 shows adsorption curves of noble gases (Ar, Kr, and Xe) obtained in the following conditions : $n_{0\text{Ar}} = 1.4 \times 10^{12}\ \text{m}^{-3}$ ($= 3.1 \times 10^{-9}$ Pa), $n_{0\text{Kr}} = 4.6 \times 10^{11}\ \text{m}^{-3}$ ($= 1.0 \times 10^{-9}$ Pa), $n_{0\text{Xe}} = 3.5 \times 10^{10}\ \text{m}^{-3}$ ($= 7.7 \times 10^{-11}$ Pa), $V = 2.9 \times 10^{-3}\ \text{m}^3$, where n_0 is the number of atoms per unit volume in the vacuum line before adsorbing the gas on the cold trap and V is the volume of the

Fig. 1. Schematic diagram of the system used for this report. CT-1, CT-2: cold trap. CT-1 contained activated charcoal. CT-2 contained a filter element (Nupro Co.) made of sintered $0.5\ \mu\text{m}$ stainless steel powder. In this report, only CT-2 was used for experiment. $V_{p1} = 3.6 \times 10^{-4}\ \text{m}^3$, $V_{p2} = 6.7 \times 10^{-4}\ \text{m}^3$, and $V_{\text{Mass}} = 2.2 \times 10^{-3}\ \text{m}^3$.

Fig. 2. Adsorption curve of Ar, Kr, and Xe for a sintered stainless steel element. The vertical axis show the fraction of the released noble gas, and the horizontal axis is the temperature of the adsorbent. The solid line was obtained by the model proposed. The adsorption energy ϵ and C_M were determined from the least squares method (see the text).

Fig. 3. Adsorption curves of Kr and Xe under two volume conditions; (S) $V=2.9 \times 10^{-3} \text{ m}^3$ and (L) $V=3.2 \times 10^{-3} \text{ m}^3$. The temperature shift of the Xe curves is slightly larger than that of Kr curves. The temperature shift at the half gas-release fraction is 2.2 K for Kr and 4.6 K for Xe, respectively.

vacuum line (we also give the partial pressure). We obtained the effective separation temperature of Kr from Ar (100 K) and Xe from Kr (120 K).

To examine the effect of gas-release volume (V) on the adsorption curves, we made adsorption experiments for Kr and Xe using two different volumes of the vacuum line (see Fig. 1): Volume L = $V_{P1} + V_{P2} + V_{\text{Mass}} = 3.2 \times 10^{-3} \text{ m}^3$, Volume S = $V_{P2} + V_{\text{Mass}} = 2.9 \times 10^{-3} \text{ m}^3$ (Fig. 3). The adsorption curve shifted to a higher temperature when we used a smaller gas-release volume. The temperature at the half gas-released fraction ($T_{1/2}$) for

Fig. 4. The adsorption curve of Ar for six initial condition of pressures: (a) $n_0 = 1.5 \times 10^{14} \text{ m}^{-3} (= 3.4 \times 10^{-7} \text{ Pa})$, (b) $n_0 = 5.3 \times 10^{13} \text{ m}^{-3} (= 1.2 \times 10^{-7} \text{ Pa})$, (c) $n_0 = 1.8 \times 10^{13} \text{ m}^{-3} (= 4.0 \times 10^{-8} \text{ Pa})$, (d) $n_0 = 6.4 \times 10^{12} \text{ m}^{-3} (= 1.4 \times 10^{-8} \text{ Pa})$, (e) $n_0 = 2.2 \times 10^{12} \text{ m}^{-3} (= 4.9 \times 10^{-9} \text{ Pa})$, and (f) $n_0 = 1.4 \times 10^{12} \text{ m}^{-3} (= 3.1 \times 10^{-9} \text{ Pa})$. The solid lines are not the curves fitting by the theoretical model. The adsorption curve shifts to a higher temperature with decreasing the pressure. As the temperature controller did not work well at the temperature between 77 and 85 K, the temperature was increased from 85 K.

Kr was 105.51 K for the large volume L and 107.73 K for the smaller volume S, respectively. Similarly, the temperature $T_{1/2}$ for Xe was 136.27 K and 140.84 K, respectively. Therefore, the temperature shift at the half gas-release fraction is 2.2 K for Kr and 4.6 K for Xe, respectively. This means that the temperature shift of Xe adsorption is larger than that of Kr. Similar experiments were carried out for Ar, but we could not observe clear differences for adsorption curves with the two conditions. The cause of these will be stated in the next section.

We noticed that the adsorption curve depends on n_0 for Ar. To understand the effect of n_0 , adsorption experiments were carried out for Ar in the following six initial pressure conditions: (a) $n_0 = 1.5 \times 10^{14} \text{ m}^{-3} (= 3.4 \times 10^{-7} \text{ Pa})$, (b) $n_0 = 5.3 \times 10^{13} \text{ m}^{-3} (= 1.2 \times 10^{-7} \text{ Pa})$, (c) $n_0 = 1.8 \times 10^{13} \text{ m}^{-3} (= 4.0 \times 10^{-8} \text{ Pa})$, (d) $n_0 = 6.4 \times 10^{12} \text{ m}^{-3} (= 1.4 \times 10^{-8} \text{ Pa})$, (e) $n_0 = 2.2 \times 10^{12} \text{ m}^{-3} (= 4.9 \times 10^{-9} \text{ Pa})$ and (f) $n_0 = 1.4 \times 10^{12} \text{ m}^{-3} (= 3.1 \times 10^{-9} \text{ Pa})$ (Fig. 4). The adsorption curve of (f) is the same one as that in Fig. 2. The adsorption curve shifted to a higher temperature for a lower pressure (small n_0). Similar experiments were made for Kr and Xe, but there were no effective differences for Kr and Xe curves.

3. Theoretical Model and Its Implication

In this chapter, we make theoretical considerations based on a simple adsorption model for better understanding the experimental observations and for obtaining conditions for more efficient noble gas separation.

It is assumed that the temperature of the vacuum line (T_v) is constant and is not

affected by the temperature of adsorbent (T), that the volume of the cold trap is negligibly small compared with that of the vacuum line (V), and that the velocity of gas atoms is controlled only by the temperature of the vacuum line. We define σ as the number of the adsorbed atoms per unit area. Now for σ , we have an equation⁵⁾

$$\frac{d\sigma}{dt} = \frac{1}{4} n v s_p - \frac{\sigma}{\tau} \quad (1)$$

where n is the number of atoms per unit volume in the vacuum line, v is the mean velocity of atoms, τ is the mean life time against desorption, and s_p is the condensation coefficient which is defined as follows:

$$s_p = \frac{N_{\text{adsorption}}}{N_{\text{collision}}}$$

where $N_{\text{collision}}$ is the number of atoms colliding the adsorbent during unit time and $N_{\text{adsorption}}$ is the number of the newly adsorbed atoms during unit time. If we assume that the number of atoms is preserved during the measurement, we can get

$$\sigma S + nV = n_0 V$$

where n_0 is the number of atoms per unit volume in vacuum line before adsorbing the gas on the cold trap and S is the surface area of the adsorbent. Then we obtain

$$\sigma = \frac{(n_0 - n)V}{S} \quad (2)$$

$$\frac{d\sigma}{dt} = - \frac{V}{S} \frac{dn}{dt} \quad (3)$$

Using Eqs. (2) and (3), Eq. (1) can be rewritten as follows:

$$\frac{dn}{dt} = - \left(\frac{1}{4} v s_p \frac{S}{V} + \frac{1}{\tau} \right) n + \frac{n_0}{\tau} \quad (4)$$

This equation is called Langmuir adsorptive equation.⁶⁾ At equilibrium, we get from $dn/dt=0$,

$$\frac{n}{n_0} = \frac{1}{1 + \frac{1}{4} v s_p \frac{S}{V} \tau} = \frac{1}{1 + C_M \tau} \quad (5)$$

where

$$C_M \equiv \frac{1}{4} v s_p \frac{S}{V} \quad (6)$$

The mean velocity v is given from the molecular dynamics as

$$v = \sqrt{\frac{8RT_v}{\pi M}} \quad (7)$$

where R is the gas constant and M is the molecular weight of the gas.

We use the following equation for τ ,⁷⁾

$$\tau = \frac{h}{kT} \exp\left(-\frac{\epsilon}{kT}\right) \quad (8)$$

where h is the Planck constant, k is the Boltzmann constant, and ϵ is the adsorption energy per atom which is negative relative to the gas phase.

The unknown parameters in Eq. (5) are ϵ and C_M . The parameter ϵ is closely related to the slope and temperature range of the absorption curve, while C_M is only a function of V in typical experimental conditions and has only a small effect on the adsorption

curve. The adsorption energy ε can be roughly estimated using only the slope at the half gas-release fraction, while the parameter C_M is calculated from the time variation of the gas-release fraction. Then we can determine the value ε and C_M , as they are close to the rough estimates, by fitting Eq. (5) to the experimental data with the least square method. The adsorption energies for Ar, Kr, and Xe are obtained from the data shown in Figs. 2 and 3 as $|\varepsilon_{Ar}| = 4.0 \times 10^{-20} \text{ J}$, $|\varepsilon_{Kr}| = (4.80 \pm 0.04) \times 10^{-20} \text{ J}$ and $|\varepsilon_{Xe}| = (6.35 \pm 0.10) \times 10^{-20} \text{ J}$. In a similar way, the adsorption energy for the activated charcoal are calculated from the data of Honda *et al.* (1993)³⁾ as $|\varepsilon_{Kr}| = 4.5 \times 10^{-20} \text{ J}$ and $|\varepsilon_{Xe}| = 6.5 \times 10^{-20} \text{ J}$, or from Podosek *et al.* (1981)⁷⁾ as $|\varepsilon_{Kr}| = 3.4 \times 10^{-20} \text{ J}$ and $|\varepsilon_{Xe}| = 5.2 \times 10^{-20} \text{ J}$. The ε values for the sintered stainless steel obtained in this study are compatible with those for the activated charcoal.

Equations (5) and (6) indicate that a small V gives a large C_M and hence a small n/n_0 , which means the adsorption curve will be shifted to a higher temperature. Our result (Fig. 3) agrees well with this prediction.

Let us consider the effect of volume V on the temperature shift of adsorption curves for individual noble gases. Assuming that the same ratio n/n_0 can be obtained for the different (V, T) and (V', T') , respectively, then we obtain

$$\frac{1}{1 + \frac{1}{4} v_{Sp} \frac{S}{V} \frac{h}{kT} e^{-|\varepsilon/kT|}} = \frac{1}{1 + \frac{1}{4} v_{Sp} \frac{S}{V'} \frac{h}{kT'} e^{-|\varepsilon/kT'|}}$$

Assuming that s_p is constant for temperatures at this range, we get

$$\frac{V'T'}{VT} \exp \left\{ - \left(\frac{1}{T} - \frac{1}{T'} \right) \frac{\varepsilon}{k} \right\} = 1 \quad (9)$$

$$\ln \left(\frac{V'}{V} \right) + \ln \left(\frac{T'}{T} \right) + \left(\frac{1}{T} - \frac{1}{T'} \right) \frac{|\varepsilon|}{k} = 0 \quad (T' > T, V' < V)$$

Putting $\Delta T = T' - T$, assuming $\Delta T/T \ll 1$ and neglecting higher powers of $\Delta T/T$, we get

$$\begin{aligned} \ln \left(\frac{V'}{V} \right) + \frac{\Delta T}{T} \left(1 + \frac{|\varepsilon|}{kT} \right) &= 0 \\ \Delta T &= T \frac{\ln(V/V')}{1 + \frac{|\varepsilon|}{kT}} = g(T) \cdot \ln \left(\frac{V}{V'} \right) \end{aligned} \quad (10)$$

where

$$g(T) \equiv T \cdot \frac{1}{1 + \frac{|\varepsilon|}{kT}} \quad (11)$$

We applied our experimental results to Eq. (10). If we use the temperature $T_{1/2}$ as that at the half gas-release fraction: $T_{1/2Ar} = 89.1 \text{ K}$, $T_{1/2Kr} = 107.7 \text{ K}$, and $T_{1/2Xe} = 140.8 \text{ K}$, we obtain $g(T_{1/2})$ as $g_{Ar}(T_{1/2}) = 2.7 \text{ K}$, $g_{Kr}(T_{1/2}) = 3.2 \text{ K}$ and $g_{Xe}(T_{1/2}) = 4.1 \text{ K}$. Therefore, we get the following relation,

$$g_{Ar}(T_{1/2}) < g_{Kr}(T_{1/2}) < g_{Xe}(T_{1/2}) \quad (12)$$

This means that the temperature shift by using a small volume would be larger for a heavier gas in qualitative accordance with the results as shown in Fig. 3. The observed temperature shift of Xe adsorption is larger than that of Kr (Fig. 3), and there was no significant shift of adsorption curves for Ar. Strictly speaking, there is a quantitative

difference between the temperature shift ΔT observed at the experiment and that obtained from Eq. (10). The observed temperature shift is 2.2 K for Kr and 4.6 K for Xe, respectively, while the calculated ΔT is 0.32 K for Kr and 0.41 K for Xe, respectively. These differences may be caused by the definition of the mean life time against desorption. In Eq. (9), the exponent has a great influence on $g(T)$. Therefore, the value $g(T)$ strongly depends on τ . However, we need not to get the accurate form for the mean life time τ . It is good enough to conclude the use of a small volume V is efficient for noble gas separation.

The above calculation is based on the assumption that the condensation coefficient s_p does not depend on the total pressure nor the temperature. However s_p may depend on the number of the adsorbed atoms when the total pressure is very high, because the number of the adsorption sites on the surface of adsorbent is limited. In such a case, we may write

$$s_p = 1 - \frac{\sigma}{\xi} \quad (13)$$

where ξ is the maximum number of the adsorbed atoms per unit area on the adsorbent surface. Using Eqs. (2) and (13) can be rewritten as follows:

$$s_p = 1 - \frac{(n_0 - n)}{\xi} \frac{V}{S} \quad (14)$$

From Eqs. (5) and (14), we get a quadratic equation for n/n_0

$$\frac{1}{4} \frac{n_0}{\xi} v \left(\frac{n}{n_0} \right)^2 + \left\{ \frac{1}{4} v \left(\frac{S}{V} - \frac{n_0}{\xi} \right) + \frac{1}{\tau} \right\} \left(\frac{n}{n_0} \right) - \frac{1}{\tau} = 0 \quad (15)$$

Putting δ and κ as

$$\delta = (n_0/\xi)/(S/V) = \frac{n_0 V}{\xi S} \quad (16)$$

$$\kappa = \frac{1}{4} \frac{S}{V} v \tau \quad (17)$$

we obtain

$$\kappa \delta \left(\frac{n}{n_0} \right)^2 + \{ \kappa(1 - \delta) + 1 \} \left(\frac{n}{n_0} \right) - 1 = 0 \quad (18)$$

and

$$\frac{n}{n_0} = \frac{1}{2\kappa\delta} \left[\sqrt{\{ \kappa(1 - \delta) + 1 \}^2 + 4\kappa\delta} - \{ \kappa(1 - \delta) + 1 \} \right] \quad (19)$$

Assuming that $\delta \ll 1$ and neglecting higher powers of δ , we get

$$\frac{n}{n_0} = \frac{1}{\kappa + 1} \left[1 + \left(\frac{\kappa}{\kappa + 1} \right)^2 \delta \right] \quad (20)$$

Equation (20) suggests that the increase of δ would result in a higher ratio of n/n_0 . Therefore, the increase of δ , that is, the increase of n_0 and/or V leads to the shift of the curve to a lower temperature. In our experiment, this effect may be most noticeable for Ar because it is the most abundant gas in the air standard. In fact, the adsorption curve for a higher pressure is located at a lower temperature (Fig. 4). These results again agree well with the expectation from our model. However, it should be noticed that Eq. (20) gives a constant n/n_0 for a very small δ , suggesting that the adsorption curve does not depend on the pressure at very low pressures. This is the reason why there are no

significant shifts of adsorption curves for Kr and Xe depending on the total pressure. The partial pressures of Kr and Xe are very low compared to Ar in the air standard.

5. Conclusion

Our theoretical model of adsorption indicates that

- (1) The adsorption curve shifts to a higher temperature when we release a gas in a smaller volume. The temperature shift of the adsorption curve is larger for gas atoms with a higher mass. To get the clear separation of individual gases, we had better use a small volume for the gas release.
- (2) The adsorption curve would shift to a lower temperature when the gas amount of a gas is not negligible compared to the maximum number of atoms which could be adsorbed on the surface of the absorbent.

All these theoretical results are in good agreement with our experimental results of adsorption using a sintered stainless steel element.

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