Liquid-Vapor Equilibrium of Isotope Mixture under Centrifugal Force

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In order to estimate the efficiency of concentrating one of the isotopic compounds by distillation of the mixture under centrifugal force, a theoretical expression for liquid-vapor equilibrium of the isotopic mixture under centrifugal force was derived and a concentration factor under practical condition was estimated for actual cases.

Derivation of the Expression for the Distribution of Isotope Mixture in Liquid-Vapor Phase System under Centrifugal Force

Consider an isotopic mixture composed of N_1 molecules of isotope 1 of mass m_1 and N_2 molecules of isotope 2 of mass m_2.

If the mole fraction of isotope 1 in the mixture is denoted by x, then

$$N_1 = Nx \tag{1}$$

$$N_2 = N(1-x) \tag{2}$$

where $N = N_1 + N_2$.

Suppose that the mixture is confined in a closed box with cross section area S and height H and is placed in a field of homogeneous centrifugal force g*, the direction of which is perpendicular to the cross section.

If the densities of molecules of isotope 1 and 2 in the vapor phase at a distance h^{v} from the liquid surface are denoted by $n_{1g}^{\mathrm{v}}(h^{\mathrm{v}})$ and $n_{2g}^{\mathrm{v}}(h^{\mathrm{v}})$ respectively and those in the liquid phase by $n_{1g}^{\mathrm{l}}(h^{\mathrm{l}})$ and $n_{2g}^{\mathrm{l}}(h^{\mathrm{l}})$ respectively, and suppose that the vapor density is sufficiently low and the liquid is not compressible, then following relations hold.

$$n_{1g}^{\mathrm{v}}(h^{\mathrm{v}}) = n_{1g}^{\mathrm{v}}(0)\cdot\exp(-m_1 gh^{\mathrm{v}}/\boldsymbol{k}T) \tag{3}$$

$$n_{2g}^{\mathrm{v}}(h^{\mathrm{v}}) = n_{2g}^{\mathrm{v}}(0)\cdot\exp(-m_2 gh^{\mathrm{v}}/\boldsymbol{k}T) \tag{4}$$

$$n_{1g}^{\mathrm{l}}(h^{\mathrm{l}}) + n_{2g}^{\mathrm{l}}(h^{\mathrm{l}}) = n_{1g}^{\mathrm{l}}(0) + n_{2g}^{\mathrm{l}}(0) = N_0 = \text{const.} \tag{5}$$

$$n_{1g}^{\mathrm{l}}(h^{\mathrm{l}}) = N_0\cdot n_{1g}^{\mathrm{l}}(0)\cdot\exp(m_1 gh^{\mathrm{l}}/\boldsymbol{k}T)/\{n_{1g}^{\mathrm{l}}(0)\cdot \exp(m_1 gh^{\mathrm{l}}/\boldsymbol{k}T) + n_{2g}^{\mathrm{l}}(0)\cdot\exp(m_2 gh^{\mathrm{l}}/\boldsymbol{k}T)\} \tag{6}$$

$$n_{2g}^{\mathrm{l}}(h^{\mathrm{l}}) = N_0\cdot n_{2g}^{\mathrm{l}}(0)\cdot\exp(m_2 gh^{\mathrm{l}}/\boldsymbol{k}T)/\{(n_{1g}^{\mathrm{l}}(0) \cdot\exp(m_1 gh^{\mathrm{l}}/\boldsymbol{k}T) + n_{2g}^{\mathrm{l}}(0)\cdot\exp(m_2 gh^{\mathrm{l}}/\boldsymbol{k}T)\} \tag{7}$$

where $\boldsymbol{k}$ is the Boltzmann constant and T is the absolute temperature of the box.

If the vaporization energy of isotope 1 is assumed to be equal to that of isotope 2, then it follows that,

$$n_{1g}^{\mathrm{l}}(0) = K_T n_{1g}^{\mathrm{v}}(0) \tag{8}$$

$$n_{2g}^{\mathrm{l}}(0) = K_T n_{2g}^{\mathrm{v}}(0) \tag{9}$$

where K_T is a constant at a given temperature, T. From the principle of conservation of mass in a closed system, the following relations are obtained.

$$S\int_0^{H_g^{\mathrm{v}}} n_{1g}^{\mathrm{v}}(h^{\mathrm{v}})\mathrm{d}h_{\mathrm{v}} + S\int_0^{H_g^{\mathrm{l}}} n_{1g}^{\mathrm{l}}(h^{\mathrm{l}})\mathrm{d}h_{\mathrm{l}} = Nx \tag{10}$$

$$S\int_0^{H_g^{\mathrm{v}}} n_{2g}^{\mathrm{v}}(h^{\mathrm{v}})\mathrm{d}h_{\mathrm{v}} + S\int_0^{H_g^{\mathrm{l}}} n_{2g}^{\mathrm{l}}(h^{\mathrm{l}})\mathrm{d}h_{\mathrm{l}} = N(1-x) \tag{11}$$

where SH_g^{v} and SH_g^{l} are the volume of the space in the box occupied by the vapor and the liquid respectively at equilibrium under centrifugal force g and namely $H = H_g^{\mathrm{v}} + H_g^{\mathrm{l}}$.

If, at equilibrium, mole fraction of isotope at the interface of liquid and vapor is denoted by x_g it follows from 5 that

$$n_{1g}^{\mathrm{l}}(0) = N_0 x_g \tag{12}$$

$$n_{2g}^{\mathrm{l}}(0) = N_0(1-x_g) \tag{13}$$

then Eqs. 6 and 7 are rewritten as

$$n_{1g}^{\mathrm{l}}(h^{\mathrm{l}}) = N_0 x_g\cdot\exp(m_1 gh^{\mathrm{l}}/\boldsymbol{k}T)/ \{x_g\cdot\exp(m_1 gh^{\mathrm{l}}/\boldsymbol{k}T) + (1-x_g)\cdot\exp(m_2 gh^{\mathrm{l}}/\boldsymbol{k}T)\}$$
$$= N_0\bigg/\left[1 + \frac{1-x_g}{x_g}\cdot\exp\{(m_2-m_1)gh^{\mathrm{l}}/\boldsymbol{k}T\}\right] \tag{14}$$

$$n_{2g}^{\mathrm{l}}(h^{\mathrm{l}}) = N_0(1-x_g)\cdot\exp(m_2 gh^{\mathrm{l}}/\boldsymbol{k}T)/ \{x_g\cdot\exp(m_1 gh^{\mathrm{l}}/\boldsymbol{k}T) + (1-x_g)\cdot\exp(m_2 gh^{\mathrm{l}}/\boldsymbol{k}T)\}$$
$$= N_0\bigg/\left[1 + \frac{x_g}{1-x_g}\cdot\exp\{(m_1-m_2)gh^{\mathrm{l}}/\boldsymbol{k}T\}\right] \tag{15}$$

and from 3, 4, 8 and 9

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* For the sake of simplicity, the values of g are assumed to be constant along the direction of height.

$$n^{v}_{1g}(h^{v})=N_0/K_T\cdot x_g\cdot\exp(-m_1gh^{v}/\boldsymbol{kT}) \quad (16)$$

$$n^{v}_{2g}(h^{v})=N_0/K_T\cdot x_g\cdot\exp(-m_2gh^{v}/\boldsymbol{kT}) \quad (17)$$

Substituting 14 and 16 into 10, and 15 and 17 into 11, and integrating them, we obtain

$$\begin{aligned}Nx=N_0S\Big[&x_g/K_T\cdot\boldsymbol{kT}/m_1g\{1-\exp(-m_1gH^{v}_{g}/\boldsymbol{kT})\}\\&+H^{l}_{g}-\boldsymbol{kT}/(m_2-m_1)g\\&\times\ln\left\{\frac{1+(1-x_g)/x_g\cdot\exp((m_2-m_1)gH^{l}_{g}/\boldsymbol{kT})}{1+(1-x_g)/x_g}\right\}\Big]\end{aligned} \quad (18)$$

$$\begin{aligned}N(1-x)=N_0S\Big[&(1-x_g)/K_T\cdot\\&\boldsymbol{kT}/m_2g\{1-\exp(-m_2gH^{v}_{g}/\boldsymbol{kT})\}+H^{l}_{g}\\&-\boldsymbol{kT}/(m_1-m_2)g\\&\times\ln\left\{\frac{1+x_g/(1-x_g)\cdot\exp((m_1-m_2(gH^{l}_{g}/\boldsymbol{kT})}{1+x_g/(1-x_g)}\right\}\Big]\end{aligned} \quad (19)$$

Calculation of Concentration Factor for Actual Cases

Now, the change of composition of isotope in the mixture by distillation under centrifugal force will be considered. When $g=0$, Eqs. 18 and 19 become

$$Nx=N_0Sx_0(1/K_T\cdot H^{v}_{0}+H^{l}_{0}) \quad (20)$$

$$N(1-x)=N_0S(1-x_0)(1/K_T\cdot H^{v}_{0}+H^{l}_{0}) \quad (21)$$

where H^{v}_{0}, H^{l}_{0} and x_0* are the values of H^{v}_{g}, H^{l}_{g} and x_g when $g=0$ respectively. By Eqs. 18 and 19 to 20 and 21 respectively and from the relation

$$H^{l}_{0}+H^{v}_{0}=H^{l}_{g}+H^{v}_{g} \quad (22)$$

the values of x_g/x_0 may be obtained in principle. However, the exact solution of these equations is very complicated.

In order to obtain a workable formula, we may expand the logarithm of the last terms in 18 and 19 in powers of $(m_2-m_1)gH^{l}_{g}/\boldsymbol{kT}$, and the following relations are obtained

$$\begin{aligned}&x_g/K_T\cdot[\boldsymbol{kT}/m_1g\cdot\{1-\exp(-m_1gH^{v}_{g}/\boldsymbol{kT})\}+H^{l}_{g}]\\&\quad+1/2\cdot\{(1-x_g)-(1-x_g)^2\}(m_1-m_2)gH^{l}_{g}/\boldsymbol{kT}\\&\quad+\cdots\cdots=x_0(H^{v}_{0}/K_T+H^{l}_{0})\end{aligned} \quad (23)$$

$$\begin{aligned}&(1-x_g)/K_T\cdot[\boldsymbol{kT}/m_2g\cdot\{1-\exp(-m_2gH^{v}_{g}/\boldsymbol{kT})\}\\&\quad+H^{l}_{g}]+1/2\cdot(x_g-x_g^2)(m_2-m_1)gH^{l}_{g}/\boldsymbol{kT}\\&\quad+\cdots\cdots=(1-x_0)(H^{v}_{0}/K_T+H^{l}_{0})\end{aligned} \quad (24)$$

If we assume that

$$|\,m_1-m_2\,|=3,$$
$$H^{l}_{g}\approx 0.1\text{ cm.}$$
$$g=10^7\text{ dyn.}$$
$$T\approx 300\text{°K}$$

then the order of magnitude of the second term of the left side of 23 or 24 is about $1/2\cdot|\,m_1-m_2\,|\times10^{-5}=1.5\times10^{-5}$ and can be neglected as being sufficiently small. Using the following notation

$$x_g=x_0(1+\delta) \quad (25)$$

$$H^{l}_{g}=H^{l}_{0}+\varDelta h,\ H^{v}_{g}=H^{v}_{0}-\varDelta h \quad (26)$$

and adding 23 and 24, we obtain

$$\begin{aligned}&x_0(1+\delta)\boldsymbol{kT}/m_1g\cdot[1-\exp\{-m_1g(H^{v}_{0}-\varDelta h)/\boldsymbol{kT}\}]\\&\quad+\{1-x_0(1+\delta)\}\boldsymbol{kT}/m_2g\\&\qquad\times[1-\exp\{-m_2g(H^{v}_{0}-\varDelta h)/\boldsymbol{kT}\}]-H^{v}_{0}\\&\quad=-K_T\varDelta h\end{aligned} \quad (27)$$

To obtain the approximate value of $\varDelta h$, the mixture may be assumed to be of single component of mass $\overline{m}=m_1x_0+m_2(1-x_0)$, then

$$\begin{aligned}&\boldsymbol{kT}/\overline{m}g\{1-\exp(-\overline{m}gH^{v}_{0}/\boldsymbol{kT})\cdot(1+\overline{m}g\varDelta h/\boldsymbol{kT})\}\\&\qquad-H^{v}_{0}=-K_T\varDelta h\end{aligned} \quad (28)$$

The value of $\varDelta h$ thus obtained is then substituted into 23 and 24, and we can obtain δ from the relation

$$\frac{\begin{gathered}\boldsymbol{kT}/m_1g\cdot\{1-(1+m_1g\varDelta h/\boldsymbol{kT})\exp(-m_1gH^{v}_{0})\}\\+K_T(H^{l}_{0}+\varDelta h)\end{gathered}}{\begin{gathered}\boldsymbol{kT}/m_2g\cdot\{1-(1+m_2g\varDelta h/\boldsymbol{kT})\}\exp(-m_2gH^{v}_{0})\\+K_T(H^{l}_{0}+\varDelta h)\end{gathered}}=\frac{1-x_0(1+\delta)}{(1-x_0)(1+\delta)} \quad (29)$$

Now consider the value of δ for an actual case. For example, consider UF_6 and assume that

$$m_1=350,\ m_2=353$$
$$K_T\fallingdotseq 300,\text{* } g=10^7\text{ dyn.}$$
$$T=333\text{°K},\ H^{v}_{0}+H^{l}_{0}=20\text{ cm.},\ H^{l}_{0}=0.1\text{ cm.}$$

TABLE I. VALUES OF δ, x'_g AND THE CONCENTRATION FACTOR $(x'_g-x_0)/x_0$ AS FUNCTIONS OF ORIGINAL CONCENTRATION x_0 OF $^{235}UF_6$ IN $^{238}UF_6-{}^{235}UF_6$ MIXTURE WITH $g=10^7$ dyn., $H=20$ cm. AND $H^{l}_{0}=0.1$ cm.

x_0	δ $\times10^{-3}$	x'_g	$(x'_g-x_0)/x_0$ %
0.01	−0.95	0.010205	2.05
0.1	−0.87	0.10186	1.86
0.2	−0.77	0.20330	1.65
0.3	−0.67	0.30432	1.44
0.4	−0.58	0.40493	1.23
0.5	−0.48	0.50513	1.03
0.6	−0.39	0.60491	0.82
0.7	−0.29	0.70429	0.61
0.8	−0.19	0.80326	0.41
0.9	−0.10	0.90183	0.20
1.0	0	1.0	0

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* By dividing 20 by 21, it follows that $x_0=x$

* The vapor is assumed to be an ideal gas, and the molar volume of vapor of 22.4 l. is divided by molar volume of UF_6 in liquid state 75.4 cc., to obtain 22.4/0.0754 =297.

and δ are calculated for $x_0=0.01$, 0.05, 0.1 and 0.9 and are shown in Table I. Using these values of δ we can calculate the composition of the isotope mixture at the top of the box. The composition x_g' thus obtained is also shown in Table I. The concentration factors x_g'/x_0 are about 1.02 and the concentration of the isotope may become quite efficient by the proper design of an apparatus for successive distillation.

Summary

Expressions for the distribution of the isotope mixture in liquid-vapor phase system under centrifugal force were derived. By the use of these expressions, the efficiency of the isotope concentration was estimated for actual cases under accessible conditions. It was found that an efficient concentration of the isotope from their mixture was possible by the proper design of an apparatus for successive distillation.

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