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DIFFUSION ENTROPY AND THEORETICAL SEPARATIVE

WORK FOR GAS MIXTURES WITH VARIABLE

CONCENTRATION

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The entropy of mixing and the minimum separative work of a gas mixture with fixed composition per kmole of a component are studied. The entropy of diffusion and the theoretical separative work per kmole of a component in the concentration range of the component are determined for a limited mass of the mixture, when the separation process proceeds with variable concentration.

Entropy of mixing and separative work per kmole of the mixture. In technology it is often necessary to separate gas mixtures. Thus oxygen and nitrogen as well as inert gases (neon, krypton, and xenon) present in them with low (up to $z = 10^{-6}$) concentrations are obtained from air. The development of nuclear power has raised the problem of separating uranium isotopes for enrichment of nuclear fuel. Helium is produced by extraction from natural gas.

The minimum separative work of a mixture of gases is determined from the increase in the entropy accompanying irreversible mixing of ideal gases under identical pressure and temperature. According to Gibbs, the increase in entropy accompanying irreversible mixing is equal to the entropy of mixing per kmole of the mixture [1]:

$$\Delta s_{\text{mixing}}^m R (z_B \ln 1/z_B + z_A \ln 1/z_A). \quad (1)$$

Hence the minimum separative work of a gas mixture with a constant composition at temperature T (in K) is

$$l_{\text{mixing}}^m T \Delta s_{\text{mixing}}^m \quad (2)$$

For a two-component mixture the entropy of mixing and the minimum separative work, which is proportional to the entropy of mixing, are usually given as functions of the concentration z , as done in Fig. 1 (dashed curve). It should be noted that the actual separative work of a mixture is, as a rule, several times greater than the indicated minimum. This indicates that other irreversible losses are also present. This dependence also gives the impression that for low concentration of one component the separative work of a mixture decreases appreciably and approaches zero, though in reality at low concentrations of the component the separation work which must be performed in order to obtain the component increases sharply. This impression results from the fact that the dashed curve in Fig. 1 is always constructed per kmole of the mixture, even though when substances are obtained from

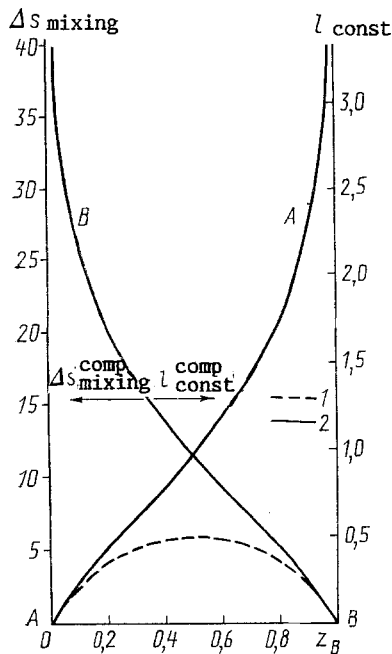


Fig. 1. Entropy of mixing Δs_{mix} , kJ/(K·kmole), and minimum separative work l_{const} , kW·h/kmole, at 300 K per kmole of the mixture (1) and per kmole of the component (2).

a mixture it is the separative work per kmole of the required component that must be determined, and the required amount of the starting mixture increases inversely as the concentration of the separated component decreases.

Entropy of mixing and separative work per kmole of the component. Dividing the entropy of mixing (1) by the molar fraction of the component B we find

$$\Delta s_{\text{mixing}}^{\text{comp}} R \left(\ln \frac{1}{z} + \frac{1-z}{z} \ln \frac{1}{1-z} \right). \quad (3)$$

Correspondingly, the minimum separative work of a mixture with a constant composition per kmole of the component is

$$l_{\text{const}}^{\text{comp}} = T \Delta s_{\text{mixing}}^{\text{comp}} \quad (4)$$

The entropy of mixing and the minimum separative work of the mixture per kmole of the component as functions of the concentration of the component in the mixture are shown in Fig. 1 (solid lines) and Table 1. Of course, in numerical calculations the separative work is always found per kmole of the component, but its dependence on the concentration of the component was never analyzed. Meanwhile, from formula (3) and the solid curves in Fig. 1 it is clear that the minimum separative work of an ideal gas mixture per kmole of the component is all the larger the smaller the concentration of the component in the mixture, and in addition it increases from zero as $z \rightarrow 1$ and approaches infinity as $z \rightarrow 0$.

We underscore the fact that the formula (1) for the entropy of mixing and therefore the formula (2) for the minimum separative work were derived under the condition that the composition of the mixture remain constant in the process of mixing and also separation of the mixture. The latter condition can be satisfied when the available quantity of the mixture available is very large. In particular, it can be satisfied when different gases are separated directly from atmospheric air.

The formula (3) makes it possible to find the separative work, determined by the first term, for the component being obtained and the work, determined by the second term, which must be performed to compress the remaining mixture to the initial pressure.

The composition of many mixtures, however, changes in the process of separation of one of the components. For example, in the case of the enrichment of natural nuclear fuel, con-

TABLE 1. Entropy of Mixing and Minimum Separative Work of a Gas Mixture with Constant Concentration z and $T = 300$ K per kmole of the Mixture and per kmole of the Component

Molar fraction, z	ΔS_{mix}^m , kJ/(K·kmole of the mixture)	$\Delta S_{\text{mix}}^{\text{comp}}$, kJ/(K·kmole of the component)	l_{const}^m , kW·h/kmole of the mixture	$l_{\text{const}}^{\text{comp}}$, kW·h/kmole of the component
1,0	0,000	0,000	0,000	0,000
0,9	2,703	3,003	0,225	0,250
0,8	4,160	5,201	0,347	0,433
0,7	5,079	7,256	0,423	0,605
0,6	5,596	9,326	0,466	0,777
0,5	5,763	11,53	0,480	0,960
0,4	5,596	13,99	0,466	1,166
0,3	5,079	16,93	0,423	1,411
0,2	4,160	20,80	0,347	1,733
0,1	2,703	27,03	0,225	2,252
0,08	2,318	28,97	0,193	2,414
0,06	1,887	31,45	0,157	2,621
0,04	1,396	34,91	0,116	2,909
0,02	0,815	40,75	0,068	3,392
0,01	0,466	46,56	0,039	3,880
10^{-3}	0,066	65,74	0,005	5,479
10^{-4}	0,008	84,89	0,001	7,074
10^{-5}	0,001	104,0	0,000	8,670
10^{-6}	0,000	123,2	0,000	10,27
10^{-7}	0,000	142,4	0,000	11,86
10^{-8}	0,000	161,6	0,000	13,46

taining only $z_1 = 0.007$ of the fissioning uranium isotope ${}_{92}^{235}\text{U}$, up to the concentration $z_2 = 0.05$ as a result of the depletion of the other, more abundant component, which is dumped when $z_3 = 0.002$, the ${}_{92}^{235}\text{U}$ concentration in the starting mixture of UF_6 gases decreases by a factor of 3.5 in the process of separation of natural uranium isotopes. The concentration changes analogously when limited quantities of other mixtures are separated.

Diffusion entropy and separative work per kmole of the component under conditions of variable concentration. The fact that, as shown above, the separative work per kmole of the component changes significantly as a function of the concentration of a component of the mixture makes it necessary to investigate the theoretical separative work of a gas mixture with variable concentration of the component of the mixture [2], when the local entropy of mixing is a function of the instantaneous concentration in the vessel or along the flow.

In thermodynamics this problem can be compared with the case of supplying heat to a process at variable temperature, when the concept of the mean integral temperature at which heat is supplied is employed.

We study the simplest case of variable concentration with irreversible mixing of two different gases under the same pressure and temperature in a volume partitioned by a barrier containing small openings. Then gas A will gradually diffuse into the volume containing gas B and gas B will gradually diffuse into the volume containing gas A until the concentrations of the gases in both parts of the volume gradually become equal, changing from zero to z and from 1 to z .

We term diffusion entropy the increase in entropy at constant temperature and pressure in the irreversible process in which the concentration changes on mixing from the initial state of pure components to equilibrium. We shall determine the diffusion entropy from the equation per kmole of the component as the mean integral value in the concentration range from 0 to z :

$$\Delta_{\text{diff}}^{\text{comp}} = \frac{R}{z} \int_0^z \left(\ln \frac{1}{z} + \frac{1-z}{z} \ln \frac{1}{1-z} \right) dz. \quad (5)$$

Then we find for the increase in the entropy of component B

$$- \int_0^z \ln z dz = -z \ln z + z, \quad (6)$$

and for the second component A we find the increase in the entropy from the second term in (5) in the form of a sum of two integrals, which individually do not represent explicit

TABLE 2. Diffusion Entropy and Theoretical Separative Work with Variable Concentration from z to 0 and $T = 300$ K per kmole of Mixture and per kmole of Component

Molar fraction z	ΔS_{diff}^m , kJ/(K·kmole of mixture)	$\Delta S_{\text{diff}}^{\text{comp}}$, kJ/(K·mole of the component)	l_{var}^m , kW·h/kmole of the mixture	$l_{\text{var}}^{\text{comp}}$, kW·h/kmole of the component	l_{sep}^B , kW·h/(kmole of the component)
1,0	13,68	13,68	1,140	1,140	0,693
0,9	13,51	15,01	1,126	1,251	0,766
0,8	13,10	16,37	1,091	1,364	0,848
0,7	12,47	17,82	1,039	1,485	0,940
0,6	12,13	19,38	1,010	1,615	1,047
0,5	10,60	21,20	0,883	1,767	1,173
0,4	9,330	23,32	0,777	1,944	1,328
0,3	7,790	25,97	0,649	2,164	1,527
0,2	5,915	29,57	0,493	2,465	1,808
0,10	3,556	35,56	0,296	2,963	2,288
0,08	3,000	37,46	0,250	3,122	2,443
0,06	2,400	39,89	0,200	3,325	2,642
0,04	1,728	43,31	0,144	3,609	2,923
0,02	0,984	49,11	0,082	4,093	3,403
0,01	0,552	54,90	0,046	4,575	3,882
10^{-3}	0,072	74,06	0,006	6,172	5,479
10^{-4}	0,012	93,20	0,001	7,767	7,074
10^{-5}	0,001	112,4	0,000	9,363	8,670
10^{-6}	0,000	131,5	0,000	10,96	10,27
10^{-7}	0,000	150,7	0,000	12,56	11,86
10^{-8}	0,000	169,8	0,000	14,15	13,46

physical quantities: the first integral is

$$\int_0^z \ln(1-z) dz = -(1-z) \ln(1-z) - z \quad (7)$$

and the second integral is

$$-\int_0^z \frac{1}{z} \ln(1-z) dz = \int_0^z \left(1 + \frac{z}{2} + \frac{z^2}{3} + \dots\right) dz = z + \frac{z^2}{4} + \frac{z^3}{9} + \dots \quad (8)$$

Substituting these expressions into Eq. (5), we obtain after cancelling the mean integral diffusion entropy per kmole of the component with variable concentration of the mixture from 0 to z :

$$\Delta S_{\text{diff}}^{\text{comp}} = R \left(\ln \frac{1}{z} + \frac{1-z}{z} \ln \frac{1}{1-z} + 1 + \frac{z}{4} + \frac{z^2}{9} + \dots \right). \quad (9)$$

Comparing Eqs. (3) and (9) we find that the first two terms of the mean integral diffusion entropy correspond to the entropy of mixing per kmole of the component, while at $z = 0$ the series is equal to 1 and at $z = 1$ the series converges to the value

$$1 + 1/4 + 1/9 + 1/16 + \dots = \pi^2/6 = 1.645... \quad (10)$$

For $0 < z < 1$ the series converges quite rapidly in the interval from 0 to 1.645 and the mean integral diffusion entropy can be determined from Eq. (9) for any change in concentration from z to 0. Then we find the theoretical separative work of a mixture with variable concentration analogously to Eq. (2) from the equation

$$l_{\text{var}}^{\text{comp}} = T \Delta S_{\text{diff}}^{\text{comp}}. \quad (11)$$

The values of the mean integral diffusion entropy and the theoretical separative work of a gas mixture with variable concentration from z to 0 are presented in Fig. 2 (solid curve 1) and Table 2 for arbitrary ideal gases.

It should be noted that in separation processes with variable concentration the mixture cannot be considered as consisting of pure substances either in the limit $z \rightarrow 0$ or in the limit $z \rightarrow 1$, but only as a mixture with a very low concentration (approaching zero) of the second component. For this reason, the separative work of a mixture with variable concentration from $z_1 \rightarrow 1$ to $z_2 \rightarrow 0$, equal to the mean integral value in the interval $0 < z < 1$ (it is determined geometrically by the average height of the dot-dashed curve B in Fig. 2), not equal to zero, as in the case of constant concentration, when $z_1 = 1$, and approaches the limit $l_{\text{var}}^{\text{comp}} = RT\pi^2/6$. For $z_1 < 1$ this work increases.

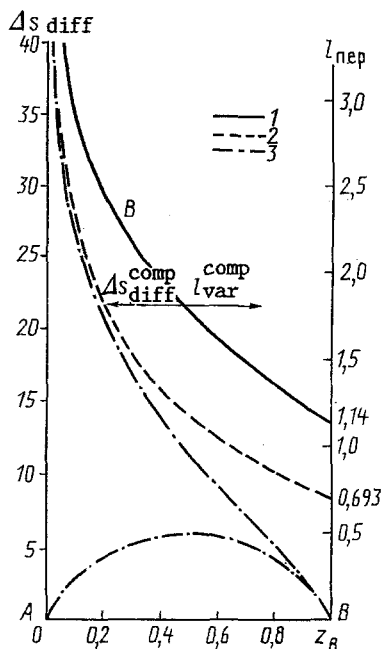


Fig. 2. Entropy of diffusion Δs_{diff} , $\text{kJ}/(\text{K}\cdot\text{mole})$, and theoretical separative work l_{var} , $\text{kW}\cdot\text{h}/\text{kmole}$, with variable concentration from z to 0 and $T = 300 \text{ K}$ per kmole of the component (1), with separation of the component (2), and with a constant concentration of the starting mixture (3).

If, however, a pure substance is considered, then the work performed by an isothermal compressor in order to transfer gas from the initial pressure p_1 to the final pressure $p_2 = 0$ is equal, according to Eq. (6), to the separative work and for $z_1 = 1$ it is equal to $l_{\text{var}}^B = RT = p v_{\mu}$ per kmole of the substance or at $T = 300 \text{ K}$ we obtain $l_{\text{var}}^B = 0.693 \text{ kW}\cdot\text{h}/\text{kmole}$, according to the dashed curve in Fig. 2 and Table 2.

The theoretical separative work per kmole of the component being separated increases rapidly as the concentration of the component in the gas mixture decreases. In this connection, we shall study the work performed when separating a mixture with variable composition with the concentration of the component changing from z_1 to z_2 . Then we find that the separative work per kmole of the component with variable concentration of the component in the mixture is equal to the difference of the products of the theoretical works of separation from z to 0 by the corresponding concentration and divided by the concentration range:

$$l_{\text{var}}^{\text{comp}} = \frac{l_{\text{var}}^{\text{comp}} z_1 - l_{\text{var}}^{\text{comp}} z_2}{z_1 - z_2} \quad (12)$$

It should be noted that the separative work with variable concentration does not depend on how the mixture was formed — by mixing with constant concentration or by diffusion with variable concentration — since the process of preparing and separating the mixture do not depend on one another and can be completed under different conditions.

We now study an example of the dependence of the theoretical work on the degree of separation of the mixture with $p^m, T^m = \text{const}$ and prescribed initial concentration z_1 . Thus if oxygen is separated from air at $T = 300 \text{ K}$ with a constant mixture concentration $z_1 = 0.21$, then the minimum separative work is $l_{\text{const}}^{\text{comp}} = 1.7 \text{ kW}\cdot\text{h}/\text{kmole}$ of the component. If air is separated from the concentration $z_1 = 0.21$ to the final concentration $z_2 = 0.06$, then the formula (12) and the data of Table 2 in this concentrative range give the following theoretical separative work:

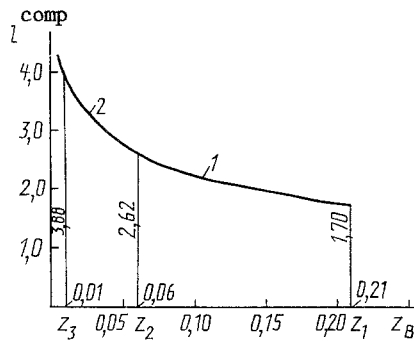


Fig. 3. Theoretical separative work of gases $l_{\text{var}}^{\text{comp}}$ in the concentration range per kmole of the component at 300 K
 $l_{0.21}^{0.06} = 2.07$; $l_{0.06}^{0.01} = 3.07$ (2) kW·h/kmole of the component.

$$l_{0.21}^{0.06 \text{ comp}} = \frac{2.43 \cdot 0.21 - 3.325 \cdot 0.06}{0.21 - 0.06} = 2.07 \text{ kW} \cdot \text{h/kmole of O}_2.$$

If we continue to separate oxygen to a molar concentration $z_3 = 0.01$, then in the additional concentration range the separative work per kmole of the component increases and is equal to

$$l_{0.06}^{0.01 \text{ comp}} = \frac{3.325 \cdot 0.06 - 4.575 \cdot 0.01}{0.06 - 0.01} = 3.07 \text{ kW} \cdot \text{h/kmole of O}_2,$$

i.e., with the higher degree of separation the specific theoretical separative work increases by a factor of 1.5. The required amount of starting mixture (air) then decreases as the ratio of the changes of the concentrations, i.e., by a factor of 1.33.

The subsequent effect of the change in the degree of separation of the mixture can be estimated with the help of the derivative

$$dl_{\text{var}}^{\text{comp}}/dz = l_{\text{cont}}^{\text{comp}} \quad (13)$$

which is equal to the minimum separative work of a mixture with constant z per kmole of the component. For the above example, according to Table 1 with $z = 0.01$ the quantity $l_{\text{const}}^{\text{comp}} = 3.88$ kW·h/kmole of O_2 , i.e., increasingly larger amounts of specific separative work $dl_{\text{var}}^{\text{comp}}/dz$ are required in order to increase the degree of separation (see Fig. 3).

The optimal degree of separation of the mixture can be determined from the fact that the effect of the degree of separation on the increase of the theoretical separative work per kmole of the component is opposite to its effect on the decrease of the concentration of the starting mixture.

Diffusion entropy and separative work per kmole of mixture with variable concentration. We shall also determine the mean integral diffusion entropy and the theoretical separative work under conditions of variable concentration per kmole of the mixture. For this we multiply the expression (9) per kmole of the component by the concentration of this component:

$$\Delta s_{\text{diff}}^{\text{m}} = R[z \ln 1/z + (1-z) \ln 1/(1-z) + z + z^2/4 + z^3/9 + \dots]. \quad (14)$$

Comparing this expression with the entropy of mixing $\Delta s_{\text{mix}}^{\text{m}}$ from (1), we find that the mean integral diffusion entropy from 0 to z with variable concentration and the entropy of mixing with constant concentration z differ by the value of the series (8)

$$\Delta s_{\text{diff}}^{\text{m}} = \Delta s_{\text{mixing}}^{\text{m}} + R(z + z^2/4 + z^3/9 + \dots). \quad (15)$$

The separative work per kmole of the mixture with variable and constant concentrations $l_{\text{var}}^{\text{m}}$ and $l_{\text{const}}^{\text{m}}$ also differ correspondingly. Figure 4 shows the indicated quantities as a function of the concentration z_B . As one can see from the figure, the mean integral diffusion entropy and the theoretical separative work with variable concentration per kmole of the mixture approach zero in the case of zero concentration and increase monotonically for

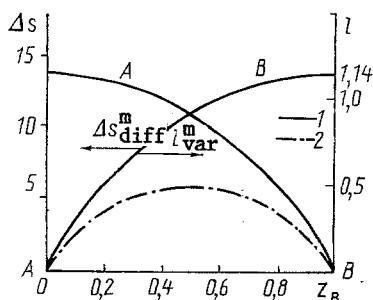


Fig. 4. Diffusion entropy Δs , kJ/(K·kmole), of the mixture and theoretical separative work ℓ of the mixture, kW·h/kmole of the mixture, with variable concentration from z to 0 at 300 K with variable concentration (1) and with constant concentration of the starting mixture (2).

each component as the concentration increases up to $z_1 \rightarrow 1$, when $\ell_{\text{var}}^m \rightarrow RT\tau^2/6 = 1.14$ kW·h/kmole of the mixture.

On the basis of the results obtained, indicating that the increase in the mean integral diffusion entropy with variable concentration is larger than the increase in the entropy of mixing of gases with constant concentration, i.e., $\Delta s_{\text{diff}}^m > \Delta s_{\text{mix}}^m$, it follows that the theoretical separative work is higher than the minimum separative work with constant concentration: $\ell_{\text{var}}^{\text{theor}} > \ell_{\text{const}}^{\text{min}}$ [3]. For this reason, in calculations of the separative work of gas mixtures it is necessary to determine whether or not the conditions of separation of the mixture correspond to constant composition in the process of separation, and in the case when the composition of the component in the process of separation is variable the theoretical separative work must be determined as indicated above. Then the ratio of the theoretical separative work to the work actually performed can give the relative efficiency of the process.

The theoretical work of extraction and separation at a different temperature of the mixture is proportional to the ratio of the absolute temperatures:

$$\ell_T / \ell_{300} = T / 300. \quad (16)$$

We studied above a binary mixture. In the case when the separative work of a given component is calculated for a multicomponent mixture all other components of the gas mixture can be lumped together as a second component. Then the results obtained for a binary mixture can be used without studying multicomponent mixtures separately.

NOTATION

A and B, components of the mixture; z , molar concentration of a component; Δs , increase of the entropy; R , gas constant; ℓ , separative work of the mixture; and T , absolute temperature. Indices: m - mixture; mix - mixing; const - constant; comp - component; diff - diffusion; and, var - variable.

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