# HOMOGENEOUS CONDENSATION OF ISOTOPIC MIXTURES EXCITED SELECTIVELY BY LASER RADIATION

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Methods of laser separation of isotopes on the basis of different physicochemical properties of excited and unexcited molecules [1] have recently been intensively investigated. In particular, the use of the influence of selective excitation on the condensation process seems to be attractive. As yet sufficiently reliable experimental data permitting comment on the selectivity of the process of molecule condensation from the gas phase are lacking. Theoretical deductions on the selectivity of the process [2] are based on the assumption that the excitation energy goes mainly over into the kinetic energy of the condensing molecule, resulting in its rapid evaporation.

1. The investigation undertaken in this paper is based on the assumptions excluding a noticeable selective effect in molecule condensation from a gas onto a macroscopic condensed phase surface. We shall consider the free path length $l$ of a migrating vibrational excitation $E_\gamma$, determined principally by the correlation radius of density fluctuations in a fluid or nonideal crystal, to be large compared to the mean intermolecular spacing $l_0$. During V–T relaxation of the excitations the energy needed for evaporation B is collected from $(E_\gamma + B)/B$ molecules to which excitation can reach in the best case $N_0 \sim (l/l_0)^{3/2}$. Since the probability that a condensing molecule will fall into this group is on the order of $E_\gamma/BN_0$, the mean probabilities w of the evaporation of molecules of the unexcited 1 and excited 2 components are referred as

$$\frac{w_2}{w_1} = \mu_2 \left(1 + \frac{E_\gamma + B}{BN_0}\right), \tag{1.1}$$

where $\mu_2$ is the initial concentration of the excited component. Here and below we consider one of the components completely excited for simplicity, while the other is completely not excited. The considerations presented apparently also refer to the case of electron excitation of one of the components with the sole difference that $l$ can be substantially greater, especially in the crystalline phase.*

Within the framework of our assumptions, molecule excitation by one of the components therefore does not result in noticeable selective effects. However, let us note that the situation is completely changed if the process of excited molecule condensation is examined in a moderate cluster of the liquid phase containing $N \ll N_0$ molecules.

For a finite cluster, it is evidently necessary to subsitute $N_0 \to N$, and the probability of evaporation of the component being excited increases. On the other hand, if $N \sim N' = E_\gamma/B$ (as is possible in the utilization of electron excitation when $E_\gamma \gg B$), ), relaxation of the excitation energy results in evaporation of the whole cluster. In other words, the clusters with size $N \leqslant N'$ being formed during homogeneous condensation do not, in practice, contain molecules of the excited component. It is understood that selectivity will gradually be lost as the nucleus grows.

2. Turning to a sequential theoretical analysis of the homogeneous condensation process with the participation of excited particles, we write the integral kinetic-balance equation [3]

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*It is possible that the results obtained are even applicable to islands of condensate on the surface.

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$$\dot{F}(\mathbf{N}, E) = \sum_{i=1,2} \int d\varepsilon \{\beta_i(\mathbf{N} - e_i, \varepsilon) F(\mathbf{N} - e_i, E - B - \varepsilon) - \\ - \alpha_i(\mathbf{N}, E, \varepsilon) F(\mathbf{N}, E) - \beta_i(\mathbf{N}, \varepsilon) F(\mathbf{N}, E) + \alpha_i(\mathbf{N} + e_i, E + B + \varepsilon, \varepsilon) F(\mathbf{N} + e_i, E + B + \varepsilon)\} \tag{2.1}$$

for the nucleus distribution function F(N, E), where $N = \{N_1, N_2\}$ is the number of molecules of the isotopic components in the nucleus, E, energy of the nucleus, $\beta_i(N, \varepsilon)$ and $\alpha_i(N, E, \varepsilon)$, molecule fluxes of the i-th component with energy ε into and out of the nucleus, respectively, and $e_i$, unit vector in the i-th direction. The expression for the condensation coefficients has the form

$$\beta_i(\mathbf{N}, \varepsilon) = \mu_i \beta(N) \rho_i(\varepsilon) \quad (i = 1, 2),$$

where $\mu_i$ are the volume concentrations of the components in the gas phase; β(N), total particle flux in the nucleus, which is proportional to the area of its surface σ; $\rho_i$ energy distributions of the component in the fluxes. As above, assuming without limiting the generality that the first component is not excited while the second is completely excited, we obtain:

$$\rho_2(\varepsilon + E_\gamma) = \rho_1(\varepsilon) \equiv \rho(\varepsilon).$$

Using the fundamental assumption on molecule deactivation during condensation, we find the evaporation coefficient $\alpha_i$ from the detailed balance condition for nonisothermal condensation. Neglecting the thermodynamic differences in the isotopes, we obtain

$$\alpha_i(\mathbf{N}, E, \varepsilon) = \frac{N_i}{N} \beta(N - 1) \rho(\varepsilon) \frac{\Phi(N - 1, E - B - \varepsilon)}{\Phi(N, E)},$$

where $\Phi(N, E) \sim \exp(-U/kT)$ is the nonisothermal equilibrium distribution function, $N = N_1 + N_2$;

$$U(N, E) = -kT \left\{ N \ln s - \frac{\alpha(T)}{kT} \sigma - \frac{(E - E_N)^2}{2\Delta_N} \right\}$$

is the minimal work of nucleus formation; s, supersaturation; α(T), surface tension coefficient; $E_N = T\alpha'(T)\sigma - \text{const}\, N$ —, total isothermal energy of the nucleus (we select const = 0);

$$\Delta_N = (kT)^2 (c_p N - T^2 \alpha''(T) \sigma)$$

($c_p$ is the fluid specific heat).

Let us solve (2.1) by the method of moments. Calculating the zeroth and first center moments of (2.1) in the concentration of the excited component, we obtain the following equation:

$$0 = \int d\varepsilon \left\{ \rho'(\varepsilon) X(N - 1, E - B - \varepsilon) - \rho(\varepsilon) \frac{\Phi'(N - 1, E - B - \varepsilon)}{\Phi'(N, E)} \times \\ \times X(N, E) - \rho'(\varepsilon) X(N, E) + \rho(\varepsilon) \frac{\Phi'(N, E)}{\Phi'(N + 1, E + B + \varepsilon)} X(N + 1, E + B + \varepsilon) \right\}, \\ 0 = \int d\varepsilon \left\{ \rho'(\varepsilon) Y(N - 1, E - B - \varepsilon) - \rho(\varepsilon) \frac{\Phi'(N - 1, E - B - \varepsilon)}{\Phi'(N, E)} \times \\ \times Y(N, E) - \rho'(\varepsilon) Y(N, E) + \rho(\varepsilon) \frac{\Phi'(N, E)}{\Phi'(N + 1, E + B + \varepsilon)} Y(N + 1, E + \\ + B + \varepsilon) - \frac{1}{N} \rho'(\varepsilon) Y(N - 1, E - B - \varepsilon) + \\ + \frac{\mu_1 \mu_2}{N} (\rho_2(\varepsilon) - \rho(\varepsilon)) X(N - 1, E - B - \varepsilon) \right\}, \tag{2.2}$$

where

$$X(N, E) = \beta(N) \sum_{\substack{N_2 \\ N_1 + N_2 = \text{const}}} F(\mathbf{N}, E);$$

$$Y(N, E) = \beta(N) \sum_{\substack{N_2 \\ N_1 + N_2 = \text{const}}} \left( \frac{N_2}{N} - \mu_2 \right) F(\mathbf{N}, E);$$

$$\Phi'(N, E) = \beta(N) \Phi(N, E); \quad \rho'(\varepsilon) = \mu_1 \rho(\varepsilon) + \mu_2 \rho_2(\varepsilon)$$

in the stationary case. For not too high supersaturations ($\ln s \lessdot 1$), it is possible to go over to a distribution continuous in N. Then to second-order accuracy, we find from (2.2)

$$-\sum_j \nabla_j A_j X + \sum_{jk} D_{jk} \nabla_j \nabla_k X = 0; \tag{2.3a}$$

$$-\sum_j \nabla_j A_j Y + \sum_{jk} D_{jk} \nabla_j \nabla_k Y - \frac{1}{N} Y - \frac{\mu_1 \delta}{N} \nabla_2 X = \frac{1}{N} \psi\left(\nabla_j Y, \nabla_j \nabla_k Y, \nabla_1 \nabla_2 X, \nabla_2^2 X\right), \tag{2.3b}$$

where

$$\begin{gathered}
\nabla = (\nabla_1, \nabla_2) = \left(\frac{\partial}{\partial N}, \frac{\partial}{\partial E}\right); \\
\mathbf{D} \equiv \begin{pmatrix} 1 & D \\ D & D^{(2)} \end{pmatrix} = \begin{pmatrix} 1 & B_0 + \delta/2 \\ B_0 + \delta/2 & B_0^{(2)} + \Delta/2 \end{pmatrix}; \\
\mathbf{A} = \begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \begin{pmatrix} \nabla_1 \ln \Phi' + B_0 \nabla_2 \ln \Phi' \\ B_0 \nabla_1 \ln \Phi' + B_0^{(2)} \nabla_2 \ln \Phi' + \delta \end{pmatrix}; \\
B_0 = \int (B + \varepsilon) \rho d\varepsilon; \quad B_0^{(2)} = \int (B + \varepsilon)^2 \rho d\varepsilon = B_0^2 + \overline{\Delta \varepsilon^2}; \\
\delta = \mu_2 \int (B + \varepsilon)(\rho_2 - \rho)\, d\varepsilon = \mu_2 E_\gamma; \quad \Delta = \mu_2 \int (B + \varepsilon)^2 (\rho_2 - \rho)\, d\varepsilon.
\end{gathered} \tag{2.4}$$

From the very beginning we shall be interested just in the asymptotic of the solution as $N \to \infty$. Then the expression for **A** from (2.4) is simplified

$$\mathbf{A} = \begin{pmatrix} \ln s - \dfrac{B_0 E}{Nd} \\ B_0 \ln s - \dfrac{B_0^{(2)} E}{Nd} + \delta \end{pmatrix}, \tag{2.5}$$

where $d \approx (kT)^2 c_p$. We also consider $E/N \ll B_0$ (slight overheating) in deriving (2.5). Now we calculate the zeroth and first moments in the energy from (2.3a)

$$-\frac{d}{dN}\left(\ln s - \overline{E} \frac{B_0}{Nd}\right) f + \frac{d^2 f}{dN^2} = 0; \tag{2.6a}$$

$$-\frac{d}{dN}\left(\overline{E} \ln s - \overline{E}^2 \frac{B_0}{Nd}\right) f + \left(B_0 \ln s - \overline{E} \frac{B_0^{(2)}}{Nd} + \delta\right) f + \frac{d^2}{dN^2} \overline{E} f - 2D \frac{d}{dN} f = 0, \tag{2.6b}$$

where

$$f = \int X(N, E)\, dE; \quad \overline{E^n} = \frac{1}{f} \int X(N, E)\, E^n dE.$$

From (2.6a) we obtain

$$\left(\ln s - \overline{E} B_0 / Nd\right) f - \frac{df}{dN} = I,$$

Where I is the total flux. Hence, under the usual boundary conditions on the boundedness of f at infinity, we find an expression for f and I in terms of the functions $\overline{E}(N)$:

$$\begin{gathered}
f = I \varphi \int_N^\infty \frac{dN}{\varphi}, \quad I = f(1) \left(\int_1^\infty \frac{dN}{\varphi}\right)^{-1}, \\
\varphi(N) = \exp\left\{\int_1^N \left(\ln s - \overline{E}(N) \frac{B_0}{Nd}\right) dN\right\},
\end{gathered} \tag{2.7}$$

which differs from that obtained in the theory of isothermal condensation [4] by an effective reduction in the supersaturation because of overheating

$$\ln s \to \ln s - \bar{E}B_0/Nd \equiv \ln s'. \tag{2.8}$$

As $N \to \infty$ $\overline{E^2} \approx \bar{E}^2$. Substituting (2.6a) into (2.6b), we obtain an equation to determine $\bar{E}(N)$

$$-\left(\ln s - \bar{E}\frac{B_0}{Nd}\right) f \frac{d\bar{E}}{dN} + \left(B_0 \ln s + \delta - \bar{E}\frac{B_0^{(2)}}{Nd}\right) f + 2\frac{d\bar{E}}{dN}\frac{df}{dN} + f\frac{d^2\bar{E}}{dN^2} - 2D\frac{df}{dN} = 0. \tag{2.9}$$

Without trying to obtain a more general solution of system (2.7), (2.9), let us note that it is satisfied by the physically unique solution

$$\bar{E} = \varkappa N, \ \varkappa = \text{const}, \tag{2.10}$$
$$f = I/\ln s' = \text{const}.$$

Here $\varkappa$ is determined from the quadratic equation

$$-\left(\ln s - \varkappa\frac{B_0}{d}\right)\varkappa + \left(B_0 \ln s + \delta - \varkappa\frac{B_0^{(2)}}{d}\right) = 0, \tag{2.11}$$

in which the lesser root should be selected

$$\varkappa = \frac{d \ln s + B_0^{(2)}}{2B_0}\left(1 - \sqrt{1 - \frac{4B_0 d\,(B_0 \ln s + \delta)}{(d \ln s + B_0^{(2)})^2}}\right), \tag{2.12}$$

since it is evident that $\varkappa$ should vanish as the heat transfer increases without limit $\overline{\Delta\varepsilon^2} \to \infty$ (isothermal limit). From the condition $\ln s' > 0$ we find a constraint on the maximum intensity of the lasting effect by using (2.8) and (2.11)

$$\delta = \mu_2 E_\gamma < \ln s \frac{\overline{\Delta\varepsilon^2}}{B_0} \equiv \delta_{\text{cr}}, \tag{2.13}$$

where condensation ceases because of overheating of the system if (2.13) is not conserved.

Let us now proceed to solve (2.3b). The right-hand side can be discarded in the asymptotic limit $N \to \infty$. Evaluating the zeroth and first energy moments as in (2.3a), while taking (2.5) into account, we obtain

$$-\frac{d}{dN}\left(\bar{y}\ln s - \overline{yE}\frac{B_0}{Nd}\right) f + \frac{d^2}{dN^2}\bar{y}f - \frac{1}{N}\bar{y}f = 0; \tag{2.14a}$$

$$-\frac{d}{dN}\left(\overline{yE}\ln s - \overline{yE^2}\frac{B_0}{Nd}\right) f + \left(\bar{y}B_0 \ln s + \bar{y}\delta - \overline{yE}\frac{B_0^{(2)}}{Nd}\right) f + \frac{d^2}{dN^2}\overline{yE}f - 2D\frac{d}{dN}\bar{y}f - \frac{1}{N}\overline{yE}f = -\frac{\mu_1\delta}{N}f, \tag{2.14b}$$

where $\bar{y} = \frac{1}{f}\int Y(N, E)\,dE$; $\overline{yE^n} = \frac{1}{f}\int Y(N, E)\,E^n dE.$

We neglect the central third-order moment of the distribution Y(N, E) to close the system of equations (2.14) by setting approximately

$$\overline{yE^2} \approx 2\bar{E}(\overline{yE} - \bar{y}\cdot\bar{E}) + \bar{y}\cdot\bar{E}^2.$$

Then, considering $\overline{E^2} \approx \bar{E}^2$ as before, and using (2.6b), (2.10), (2.11), we reduce system (2.14) after simple calculations to the form

$$\frac{d^2\bar{y}}{dN^2} - \ln s' \frac{d\bar{y}}{dN} - \frac{\bar{y}}{N} = -\frac{B_0}{d}\frac{d}{dN}\left(\frac{z}{N}\right),$$

$$\frac{d^2 z}{dN^2} - \ln s' \frac{dz}{dN} - \left(1 + \frac{B_0^{(2)} - B_0\varkappa}{d}\right)\frac{z}{N} = 2(B_0 - \varkappa)\frac{d\bar{y}}{dN} - \frac{\mu_1\delta}{N},$$

where $z = \overline{yE} - \bar{y}\cdot\bar{E}$. The solution of this system for $N \to \infty$ has the asymptotic form

$$\bar{y} = -\frac{A}{N} + O\left(\frac{1}{N^{\alpha}}\right), \quad \alpha = \min\left\{2, \frac{1}{\ln s'}\right\}, \qquad (2.15)$$

$$A = \frac{B_0\mu_1\delta}{\left(d + B_0^{(2)} - B_0\varkappa\right)(1 - \ln s')}.$$

The negative sign of $\bar{y}$ corresponds to depletion of the clusters in the excited component. Substituting (2.11) into (2.15), we obtain for the coefficient A

$$A = \frac{B_0\mu_1\delta}{B_0(B_0 + \delta) + \left(d + \overline{\Delta\varepsilon^2}\right)(1 - \ln s)} \approx \frac{\mu_1\delta}{B_0} = \mu_1\mu_2\frac{E_\gamma}{B_0}, \qquad (2.16)$$

since $d \simeq \overline{\Delta\varepsilon^2} \simeq (kT)^2$, $B_0^2 \simeq (10{-}100)\ (kT)^2$ and $\delta < \delta_{cr} < B_0$ in the absence of a gas carrier. The limit depletion of clusters in the excited component sets in, as is seen from (2.16), for

$$N \leqslant N' = \mu_1 \frac{E_\gamma}{B_0},$$

which is in complete agreement with the approximate result presented at the beginning of the paper. This agreement permits the hope that the obtained asymptotic results are valid in order of magnitude and in the domain of finite dimensions $N \geqslant N'$.

In the general case of incomplete excitation of both isotopic components, the mean concentration c(N) of the primarily excited component is determined by the expression

$$c(N) = c_0 + \frac{\theta - c_0}{\mu_1}\bar{y}(N),$$

where $c_0$ is the concentration of this component in the gas phase; $\theta$, fraction of excited particles of this component out of the total number of excited particles, which characterizes the selectivity of the excitation; $\mu_2$, $\mu_1$, as before, the total concentrations of the excited and unexcited particles of both species in the gas phase, respectively. The separation factor $\eta = c/c_0$ equals

$$1 > \eta(N) \approx 1 - \frac{(\theta - c_0)\delta}{c_0 B_0}\frac{1}{N} = 1 - \frac{\mu_2}{c_0}\frac{E_\gamma}{B_0}\frac{\theta - c_0}{N}. \qquad (2.17)$$

It is seen that incomplete excitation substantially diminishes the separation since even in the maximum depletion domain in the excitation $N \leqslant N'$, we have

$$1 > \eta > 1 - \frac{\mu_2}{c_0}(\theta - c_0).$$

The expediency of using electronic excitation for which $E_\gamma$ and $\mu_2/c_0$ are generally approximately an order of magnitude greater than for the vibrational excitation, follows from (2.17). Setting $\theta - c_0 \approx 1$, $E_\gamma/B_0 \sim 10$, $\mu_2/c_0 \sim 0.1$ and $N \simeq 20$, we obtain $\eta \simeq 0.95$ in this case.

The influence of molecule excitation on the homogeneous condensation of a mixture of isotopes has been examined in the simplest case of a spatially homogeneous system with given supersaturation. The most convenient method of realizing homogeneous condensation is apparently condensation in gas jets. The complications occurring here have not been analyzed in detail in this paper. Let us just note that the existence of a domain of values characterizing the regime of the process of the parameter $p_0{}^{d^{*0.6}}$, where $p_0$ is the initial gas pressure in the jet, and $d^*$ is the nozzle diameter in which condensation is terminated by the formation of clusters with $N \sim 20$–$30$, for which noticeable separation can be expected from (2.17), while on the other hand the fraction of fluid far from the nozzle is almost a maximum, follows from the results in [5]. These results apparently carry over to our case as well with the difference that termination of condensation in the presence of condensation corresponds to the reduction of the effective supersaturation $\ln s' = 0$, i.e., sets in for finite supersaturations $\ln s = \mu_2 E\gamma B_0/\overline{\Delta\varepsilon}^2 > 0$.

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# THEORY OF THE KINETIC COOLING OF A $CO_2$–$N_2$ MIXTURE WITH A HIGH $CO_2$ CONTENT

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Resonance absorption by $CO_2$ molecules of radiation upon the intermodal transition (100)–(001) (or (020)–(001)) leads to nonstationary cooling of the gas [1], due mainly to the flow of energy from the translational degrees of freedom into the deformation mode of the $CO_2$ as a result of the process of V–T relaxation. An investigation of the effect of kinetic cooling of carbon dioxide under the action of radiation is of interest for problems in oscillation kinetics (determination of the relaxation time, analysis of the operation of molecular gas lasers) and in the propagation of radiation through gaseous media (autonomous thermal effect).

Theoretical studies have thus far been conducted on the phenomenon of kinetic cooling for atmospheric conditions (the case of low $CO_2$ concentrations) [2, 3]. Experimental investigations have been conducted on cooling with mixtures with partial $CO_2$ concentrations of $x_{CO_2} = 10^{-3}$–$1$ [4–7] at a gas temperature of $T_0 < 400$°K. The measured values of the kinetic-cooling parameters were in satisfactory agreement with the results of numerical calculations [7, 8] performed on the basis of a "thermodynamic" model [9]. In [10] a theoretical investigation was conducted on the channel of relaxation of the state of $CO_2$ (001) which made the main contribution to the variation of gas temperature.

In the present study we obtained analytic expressions for the parameters of the cooling of a mixture of gaseous $CO_2$ and $N_2$ over wide ranges of $CO_2$ partial concentrations and of intensities of the exciting radiation; we investigated the temperature dependence of the effect in the 200–1200°K range, which enabled us to establish the temperature region in which the phenomenon of kinetic cooling exists. We also considered the problem of optimal insertion of the energy of a light pulse for cooling a molecular system.

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