Selective Sorption and Facilitated Transport of Oxygen in Porphinatocobalt-Coordinated Polymer Membranes

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ABSTRACT: Selective sorption and permeation of molecular oxygen are described for *meso*-α,α,α,α-tetrakis(*o*-pivalamidophenyl)porphinatocobalt(II) (CoP) coordinated polymer membranes (Chart I). Oxygen solubility is ca. 70 times augmented in comparison with that of nitrogen by the CoP loading in the membrane. Sorption isotherms of oxygen for the membranes are analyzed with a dual-mode sorption model to give C_C' and K. C_C' (the saturated amount of oxygen reversibly bound to the CoP sorption site) is independent of temperature and increases with the loaded CoP amount into the membrane. K (the oxygen-affinity constant of CoP) agrees with that determined spectroscopically by monitoring the CoP moiety in the membrane. Oxygen permeation through the membrane is facilitated, and the permeability is in accordance with a dual-mode transport model. Substituting the sorption parameters, C_C' and K, in the model yields diffusion constants of oxygen in the membranes.

Introduction

Gas sorption phenomena in polymers are still of great interest.[1-3] For example, sorption of condensable penetrants in glassy polymers is known to reveal abnormally high solubility for the penetrants, and its nonlinear sorption isotherms are often analyzed by a dual-mode combination of Henry's law type dissolution in the polymer and a Langmuir-type one in a frozen free volume or a microvoid in the polymers.[4,5] But in these investigations, the nature of the Langmuir sorption sites is not yet elucidated due to nonequilibrium or an unrelaxed aspect of the microvoids, plasticization of the glassy polymers by the sorbed gases, and/or microstructural heterogeneity in the polymers.

Recently we succeeded in preparing a rubbery poly(alkyl methacrylate) membrane containing an imidazole–porphinatocobalt, which binds oxygen selectively, rapidly, and reversibly and acts as a chemical sorption site or a fixed carrier of oxygen. We have reported facilitated transport or carrier-mediated transport of oxygen in the membrane,[6,7] in which the porphinatocobalt binds oxygen, thereby increasing the transport rate of oxygen relative to nitrogen in the feed stream. We discussed the oxygen transport using a dual-mode transport model,[8] where the oxygen permeability is governed by physical oxygen permeation and oxygen transport via the fixed carrier or the chemical sorption site.

$$P = k_D D_D [1 + FR/(1 + Kp_2)] \quad (1)$$

$$F = D_C/D_D, \quad R = C_C'K/k_D$$

Here, P is the permeability coefficient, k_D is the solubility coefficient for Henry's law, D_C and D_D are diffusion coefficients of oxygen via the chemical sorption site and through the polymer matrix, C_C' is the saturated oxygen-sorption amount to the site, K is the oxygen-affinity or -binding equilibrium constant of the site, and p_2 is the upstream oxygen pressure. We reported D_D, D_C, k_D, and C_C' calculated by the combination of eq 1 and the time lag equation for permeation curves. However, selective oxygen sorption behavior in these polymers has not been studied quantitatively, and the dual-mode transport parameters are to be determined by both sorption and permeation measurements.

This paper describes the selective sorption and facilitated transport of oxygen in the polymer membranes of CoP as the chemical sorption site or the fixed carrier of oxygen: *meso*-α,α,α,α-tetrakis(*o*-pivalamidophenyl)porphinatocobalt(II) (CoP) coordinated to poly(octyl methacrylate-*co*-4-vinylpyridine) or poly(octyl methacrylate-*co*-1-vinylimidazole) (Chart I). Since these polymer membranes establish oxygen sorption equilibrium rapidly under the exposed atmosphere, the gas sorption is able to be more precisely measured in comparison with that for glassy polymers. The sorption and transport behaviors of oxygen in the membranes are measured and discussed by the combination of the dual-mode sorption and transport model equation.

Experimental Section

Materials and Membrane Preparation. *meso*-α,α,α,α-Tetrakis(*o*-pivalamidophenyl)porphinatocobalt(II) (CoP) was synthesized as in ref 9. Poly(octyl methacrylate-*co*-4-vinylpyridine) (OPy) and poly(octyl methacrylate-*co*-1-vinylimidazole) (OIm) were prepared by the radical copolymerization of octyl methacrylate with 4-vinylpyridine or 1-vinylimidazole. The content of the 4-vinylpyridine or 1-vinylimidazole residue content and the molecular weight of the copolymers were determined by elemental analysis and gel permeation chromatography (with tetrahydrofuran as the solvent and polystyrene as the standard) to be 48 and 24 wt % and 1.5×10^6 and 1.2×10^6 for OPy and OIm, respectively.

A chloroform solution of the copolymer and CoP was carefully cast on a Teflon plate under an oxygen-free atmosphere, followed by drying in vacuo, to yield a transparent, homogeneously red-colored, and flexible membrane with a thickness of ca. 60 μm. A differential scanning calorimetric (DSC) thermogram of the membranes was measured with a Seiko SSG-560U. Electron probe (X-ray) microanalysis (EPM) on the cobalt ion of CoP in the membranes was measured with a JEOL JXA-733.

Gravimetric and Permeation Measurement. Sorption isotherms of oxygen and nitrogen were measured gravimetrically by a Cahn Model 2000 electrobalance set in a high-pressure chamber made of stainless steel.[5] The apparatus consists essentially of a high-pressure chamber mounted in a thermostatically controlled air bath and a gas supply system. The membrane was subjected to up to 50 atm of pressure at 45 °C

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Chart I

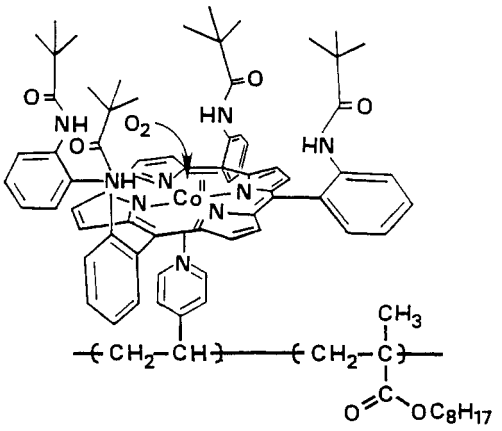

Table I
Dual-Mode Sorption Parameters of Oxygen for the CoP–OPy Membranes at 45 °C

CoP, wt %	T_g, °C	10^3K, 1/cmHg	10^4k_D, cm³ (STP)/ cm³ (polym) cmHg	$C_{C'}$, cm³ (STP)/ cm³ (polym)
0	37		4.6	
1.8	42	5.0	5.5	0.1
15	51	5.5	7.1	1.4
25	64	5.2	7.7	2.7
37	78	4.7	8.6	4.8
2.0[a]	41	5.4		

[a] Datum estimated by the spectroscopic measurement.

for sorption isotherm determination. After the given pressure was maintained for 1.5 h or more due to equilibrium of gas sorption, the weight change of the membrane was recorded. The weights of the membrane and Au wire were ca. 200 and 400 mg, respectively. Because of the large chamber volume (about 4000 cm³) and the small membrane size (ca. 0.2 cm³), sorption and desorption did not produce detectable changes in pressure. Densities of the membrane before and after to 40 atm of pressure were determined by the flotation method with a density meter (Anton Paar, DMA 02D) and magnesium chloride aqueous solution.[5]

Oxygen and nitrogen permeation coefficients for various upstream gas pressures were measured with a low-vacuum permeation apparatus (Rika Seiki Inc., Model K-315 N-01), as reported in the previous paper.[6,7]

Results and Discussion

Oxygen Binding to the CoP Moiety in the Polymer Membranes. We previously prepared CoP membranes by simply and physically dispersing the CoP coordinated with a low molecular weight nitrogenous ligand such as 1-methylimidazole in poly(alkyl methacrylate)s. However, this preparation process was often accompanied with a carrier deactivation or an irreversible oxidation of CoP to $Co^{III}P$. That is, CoP is liable to aggregate during the casting process and after oxygen exposure is converted to $Co^{III}P$, which has no oxygen-binding ability. On the other hand, the attachment of CoP onto the polymeric nitrogenous ligand provides the following advantages: (i) The fixation on the polymer chain suppresses the irreversible oxidation through the aggregation of CoP. (ii) The fixation also suppresses a phase separation of CoP even in the highly CoP-loaded membrane. The homogeneous dispersion of CoP in the membranes was confirmed by the following two results. Each membrane exhibited one glass transition temperature (T_g) as shown in Table I, which denied the presence of microphase-separated morphologies. EPM photographs of the membranes showed a uniform dispersion of the CoP cobalt ion in the membranes. (iii) While a monomeric nitrogenous ligand is slowly vaporized through the casting and evacuating of the membrane and the passage of a larger amount of gas, the polymeric one is not lost through the operations. At any rate, the active CoP–OPy and CoP–OIm membranes were relatively easily yielded by casting their solutions even under not strictly an oxygen-free atmosphere.[10]

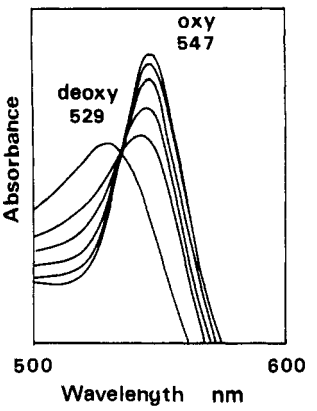

Figure 1. Visible absorption spectrum in the CoP–OPy membrane at 25 °C.

Oxygen binding to the CoP moiety in the membrane is rapid and reversible. A visible absorption spectrum of the reddish and transparent membrane is shown in Figure 1. The spectrum (λ_{max} = 529 nm) of the deoxy-CoP was changed to the spectrum with λ_{max} = 547 nm assigned to the oxy-CoP (O_2/Co = 1/1 adduct) immediately after exposure of the membrane to oxygen. The oxy–deoxy spectral change (the chemical sorption and desorption cycle of oxygen) was reversible in response to the oxygen partial pressure with isosbestic points at 477, 537, and 655 nm. The oxygen-affinity or -binding equilibrium constant (K) of the CoP moiety coordinated to the pyridine residue of OPy in the membrane was determined from this spectral measurement of the oxygen-binding equilibrium and given in Table I.

Sorption of Oxygen and Nitrogen in the Membranes. Figure 2 shows sorption isotherms of oxygen for the CoP-coordinated OPy and OIm membranes. The oxygen sorption amount is much enhanced by the introduction of CoP in the membrane. For example, the oxygen sorption amount for the CoP–OIm membrane is ca. 20 times augmented in comparison with that for the OIm control membrane and is ca. 70 times larger than that of nitrogen for CoP–Im at 7.8 cmHg. This oxygen pressure is corresponding to the pressure ($p_{1/2}O_2$ = 1/K) at which half of the CoP moiety binds oxygen. The fixed CoP moiety acts as an effective and selective oxygen sorption site in the membrane. The sorption amount of oxygen in the CoP–OIm membrane was larger than that in the CoP–OPy membrane, because of larger oxygen affinity for the CoP–OIm ($p_{1/2}O_2$ + 7.8 cmHg) than for the corresponding CoP–OPy ($p_{1/2}O_2$ = 34 cmHg).

The effect of the loaded-CoP amount on oxygen sorption isotherms for the OPy membrane is shown in Figure 3. In contrast to the nitrogen sorption isotherm, these oxygen sorption isotherms are nonlinear and seem to be in accordance with a dual-mode sorption model. The dual-mode sorption model for condensable penetrants in glassy polymers is represented by the sum of the physical dissolution described by Henry's law and the adsorption described by a Langmuir isotherm. The total amount of sorbed oxygen (C) is given by

$$C = k_D p_2 + C_H' b p_2/(1 + b p_2) \quad (2)$$

Here, k_D is the solubility coefficient in Henry's law, p_2 is

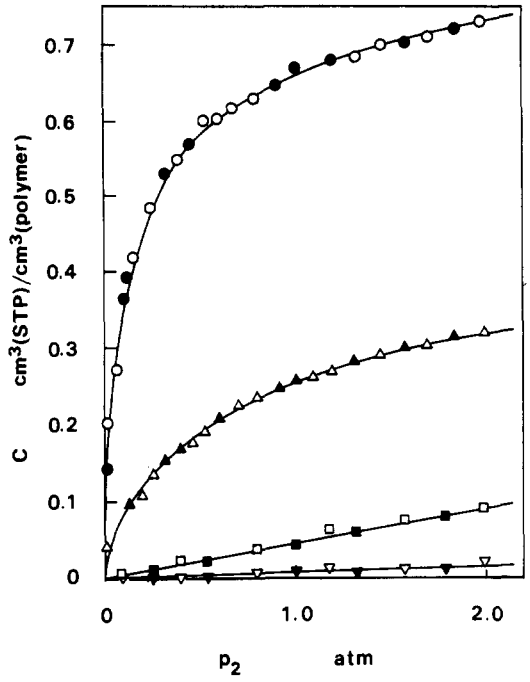

Figure 2. Sorption isotherms of oxygen and nitrogen for the CoP–OPy and CoP–OPy membranes at 25 °C. Open and solid symbols are sorption and desorption runs, respectively: (○) oxygen for CoP–OIm, (△) oxygen for CoP–OPy, (□) oxygen for OIm, and (▽) nitrogen for CoP–OIm.

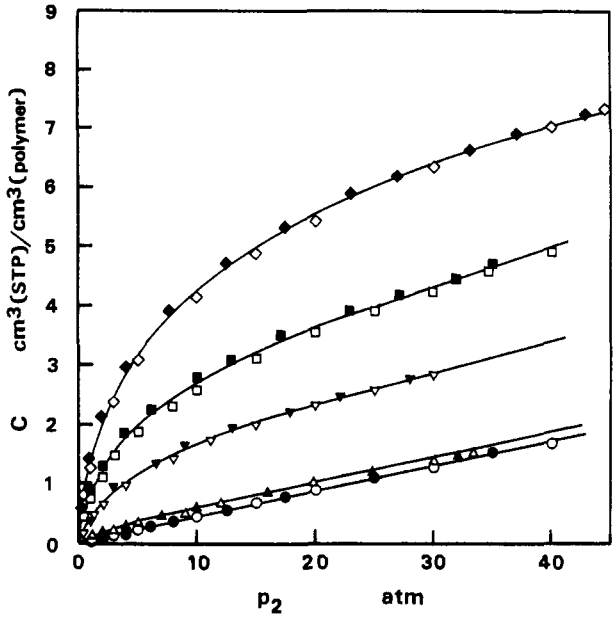

Figure 3. Sorption isotherm of oxygen for the CoP–OPy membranes at 45 °C. Open and solid symbols are sorption and desorption runs, respectively: (○) [CoP] = 0 wt %, (△) 1.8 wt %, (▽) 15 wt %, (□) 25 wt %, and (◇) 37 wt %.

the atmospheric gas pressure, b is Langmuir's affinity constant, and C_H' is Langmuir's capacitive constant for the polymer. By referring to this equation, a dual-mode model for the oxygen sorption isotherm in the CoP membrane, where the CoP acts as a specific and reversible oxygen sorption site according to the Langmuir isotherm, is converted as eq 3

$$C = k_D p_2 + C_C' K p_2/(1 + K p_2) \quad (3)$$

where C_C' is the saturated amount of oxygen reversibly bound to the sorption site CoP moiety and K is the oxygen-affinity or -binding equilibrium constant of the CoP.

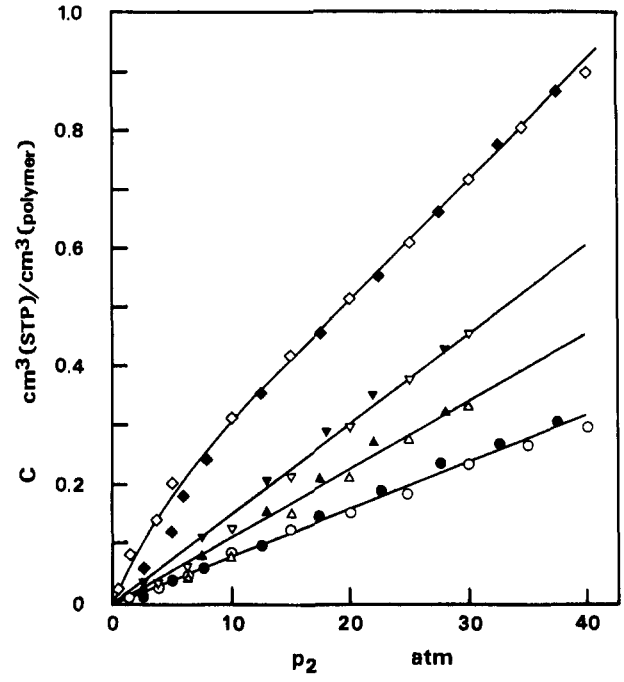

Figure 4. Sorption isotherm of nitrogen for the CoP–OPy membranes at 45 °C. Open and solid symbols are sorption and desorption runs, respectively: (○) [CoP] = 0 wt %, (△) 1.8 wt %, (▽) 15 wt %, and (◇) 37 wt %.

Table II
Dual-Mode Sorption Parameters of Nitrogen for the CoP–OPy Membrane at 45 °C

CoP, wt %	$10^3 b$, 1/cmHg	$10^4 k_D$, cm³ (STP)/cm³ (polym) cmHg	C_H' cm³ (STP)/cm³ (polym)
0		1.1	
1.8		1.7	
15		2.4	
37	1.0	2.6	0.4

The sorption isotherms were analyzed in terms of this dual-mode sorption model with nonlinear least-squares regression, to give the dual-mode sorption parameters k_D, K, and C_C' in Table I. The solid lines in Figure 3 were drawn by using the dual-mode sorption parameters given in Table I and eq 3. The measured plots agreed with the solid lines, which supports the hypothesis that the sorption behavior is represented by the dual-mode model.

In Table I, C_C' increases with the loaded-CoP amount in the membrane.[11] On the other hand, K of the CoP moiety is independent of the loaded-CoP amount and agrees with the equilibrium constant spectroscopically determined. These results support the validity of the treatment based on the dual-mode sorption model.

Figure 4 shows the sorption isotherms of nitrogen for the CoP–OPy membranes. The sorption isotherms were linear, ascribed to Henry's law, and independent of the loaded-CoP amount in the membrane, because the CoP moiety does not interact with nitrogen. k_D's of oxygen and nitrogen in Tables I and II slightly increase with the loaded-CoP amount because bulky CoP is introduced in the membrane. Physically additive Langmuir-type sorption of nitrogen in the membranes was negligible despite their slightly glassy property, probably because their T_g's (see Table I) were not much above the sorption measurement temperature.

However, the nitrogen sorption into the 37 wt % CoP-loaded membrane was nonlinear and obeyed the dual-mode sorption model (eq 2). Sorption parameters, b and C_H', were determined with nonlinear least-squares re-

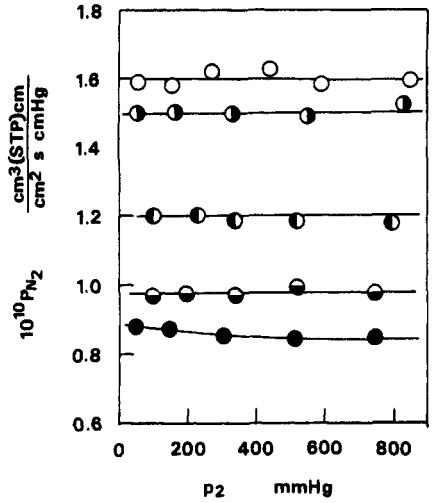

Figure 5. Effect of upstream nitrogen pressure on the nitrogen permeability coefficient for the CoP–OPy membranes at 45 °C: (○) [CoP] = 0 wt %, (◑) 1.8 wt %, (◐) 15 wt %, (◒) 25 wt %, and (●) 37 wt %.

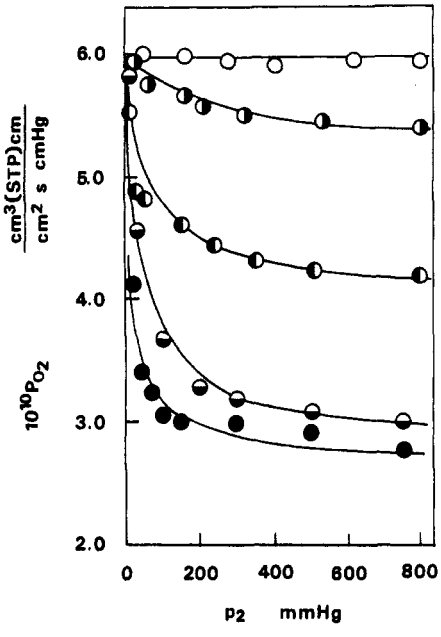

Figure 6. Effect of upstream oxygen pressure on the oxygen permeability coefficient for the CoP–OPy membranes at 45 °C: (○) [CoP] = 0 wt %, (◑) 1.8 wt %, (◐) 15 wt %, (◒) 25 wt %, and (●) 37 wt %.

gression and were given also in Table II. Langmuir's capacity (C_H') and affinity constant (b) are associated with the excess volume based on the nonequilibrium state of the polymer below T_g. The $C_H'b$ value based on the glassy property of the membrane was ca. 50 times smaller than the $C_C'K$ value contributed by the chemical sorption of oxygen to the CoP moiety in the membrane.[12] That is, the chemically selective oxygen sorption to the CoP moiety is superior to the physical oxygen sorption to a microvoid or a frozen free volume in the polymer.

Oxygen Permeation in the Membranes. Figures 5 and 6 show the effects of upstream gas pressure (p_2) on the permeability coefficient (P) in the CoP–OPy membranes. In Figure 5, the nitrogen permeability coefficient [$P(N_2)$] in the membranes is independent of $p_2(N_2)$ regardless of the loaded-CoP amount and obeys a physical permeation described by Henry's mode, because nitrogen does not interact with the CoP moiety in the membrane. However, $P(N_2)$ for the 37 wt % CoP-loaded membrane slightly depends on $p_2(N_2)$ at a low-pressure region. The membrane was glassy (T_g = 78 °C) at the permeability measurement temperature. The nitrogen permeation in this membrane was in accordance with a dual-mode transport model, just as the sorption isotherm was.

Table III
Dual-Mode Transport Parameters of Oxygen for the CoP–OPy Membrane at 45 °C

CoP, wt %	$10^7 D_D$, cm²/s	$10^8 D_C$, cm²/s
0	13	
1.8	9.1	9.9
15	3.4	3.1
25	2.7	0.89
37	2.4	0.40

The oxygen permeability coefficients [$P(O_2)$] are larger than $P(N_2)$ and markedly increased with a decreasing $p_2(N_2)$, as seen in Figure 6. This indicates that oxygen transport in the CoP–OPy membranes occurs according to a dual-mode transport represented by eq 1. The upstream pressure dependency of $P(O_2)$ was steeply enhanced for the membrane with a higher CoP-loaded amount. That is, the contribution of the CoP moiety as a fixed oxygen carrier corresponds to the loaded-CoP amount.

Dual-mode transport parameters analyzed by using eqs 1 and 3, D_D and D_C, are listed in Table III. The physical diffusion coefficient through the membrane polymer (D_D) decreases with the loaded-CoP amount because of a hardening effect of the CoP on the polymer. The diffusion coefficient of oxygen via the CoP moiety (chemical sorption or fixed carrier site) (D_C) is also reduced by the loaded-CoP amount, probably because diffusive movement of the penetrant between the carrier sites involves a physical diffusivity through the polymer.

The effect of the loaded-CoP amount or the sorption site concentration in the membrane on the permselectivity is shown in Table III. The permselectivity [$P(O_2)/P(N_2)$] increases with the sorption site concentration and shows the maximum value 8.3 for the 25 wt % CoP-loaded membrane.

Conclusion

The oxygen and nitrogen sorption study on the CoP-coordinated polymer membranes showed that a porphinatocobalt such as CoP fixed chemically within a polymer membrane acts as a selective sorption site of oxygen and enhances oxygen solubility into the polymer membrane in proportion to the loaded porphinatocobalt amount. The sorption was a rapidly reversible one, increasing the permeation rate of oxygen relative to nitrogen, but the loading of a chemical sorption site such as CoP within a membrane caused hardening of the membrane and a reduced physical diffusivity of the permeate oxygen through the membrane. Tuning of the membrane polymer structure to maintain its physical property at a constant during the loading of the sorption site is essential for both a higher oxygen permeability and a more precise discussion on the facilitated or carrier-mediated transport mechanism.

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(11) The C_C' value in Table I does not completely agree with the loaded-CoP amount probably due to partial inactivation of CoP through the membrane preparation.
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Registry No. O_2, 7782-44-7; N_2, 7727-37-9.