

Supporting Information:

Molecular order determines gas transport through smectic liquid crystalline polymer membranes with different chemical compositions

Joey Kloos^a, Nico Jansen^a, Menno Houben^a, Kitty Nijmeijer^a, Albert P.H.J.

Schenning^b, Zandrie Borneman^{a,*}

^a Membrane Materials and Processes, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

^b Stimuli-responsive Functional Materials and Devices, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

* Corresponding author: z.borneman@tue.nl

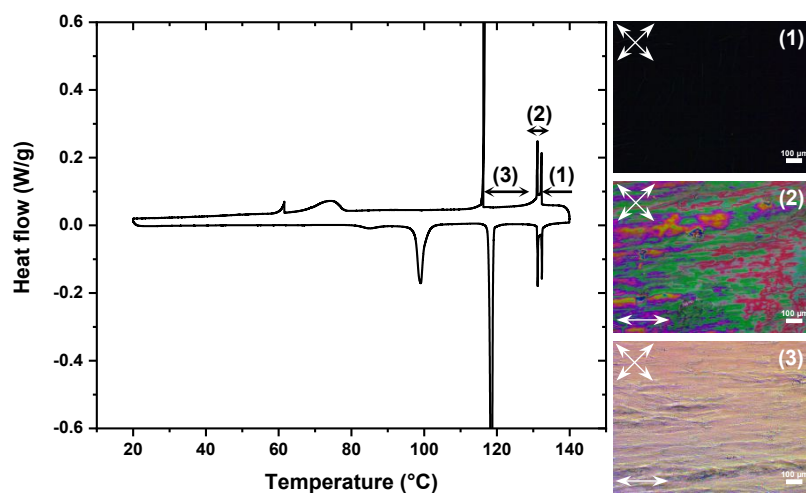


Figure S1: DSC measurement and POM images of an LC mixture with a M1/M2 composition of 0/100, a photoinitiator, and an inhibitor. Measurement was taken at a heating/cooling rate of 3 °C/minute (exothermal down). The POM images correspond to respectively isotropic (1), nematic (2), and smectic (3) phases in the DSC graph. The single arrow represents the alignment direction. The axis of the crossed polarizers are represented by the crossed arrows.

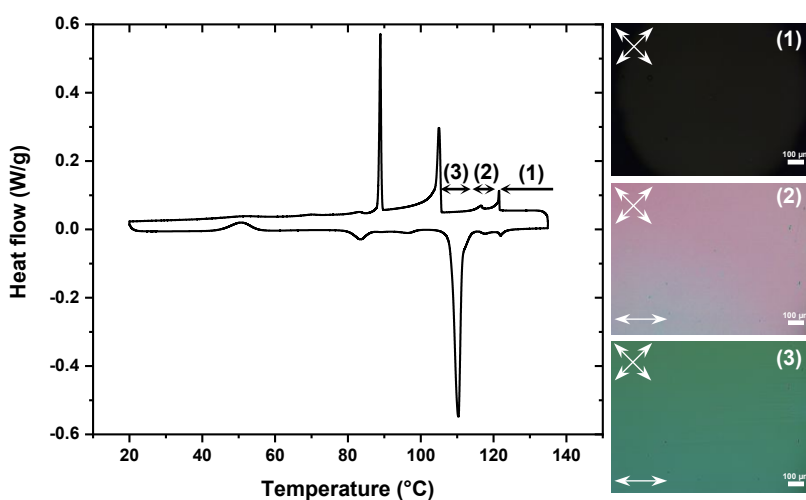


Figure S2: DSC measurement and POM images of a LC mixture with a M1/M2 composition of 30/70, a photoinitiator, and an inhibitor. Measurement was taken at a heating/cooling rate of 3 °C/minute (exothermal down). The POM images correspond to respectively isotropic (1), nematic (2), and smectic (3) phases in the DSC graph. The single arrow represents the alignment direction. The axis of the crossed polarizers are represented by the crossed arrows.

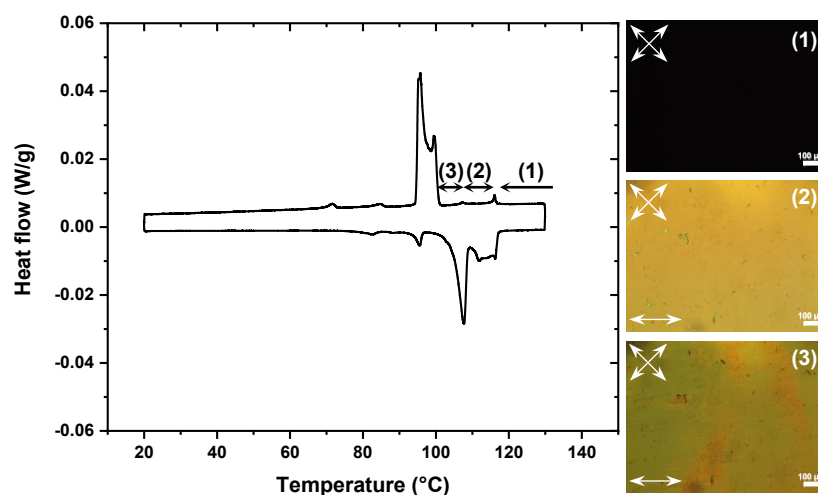


Figure S3: DSC measurement and POM images of a LC mixture with a M1/M2 composition of 50/50, a photoinitiator, and an inhibitor. Measurement was taken at a heating/cooling rate of 3 °C/minute (exothermal down). The POM images correspond to respectively isotropic (1), nematic (2), and smectic (3) phases in the DSC graph. The single arrow represents the alignment direction. The axis of the crossed polarizers are represented by the crossed arrows.

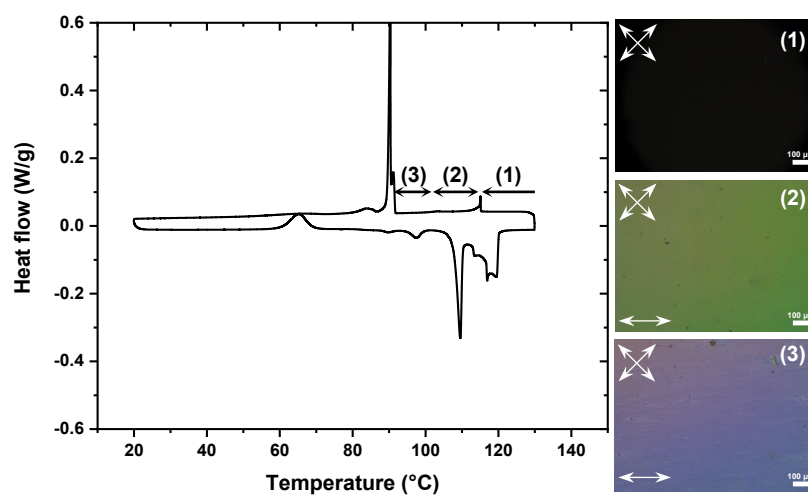


Figure S4: DSC measurement and POM images of a LC mixture with a M1/M2 composition of 60/40, a photoinitiator, and an inhibitor. Measurement was taken at a heating/cooling rate of 3 °C/minute (exothermal down). The POM images correspond to respectively isotropic (1), nematic (2), and smectic (3) phases in the DSC graph. The single arrow represents the alignment direction. The axis of the crossed polarizers are represented by the crossed arrows.

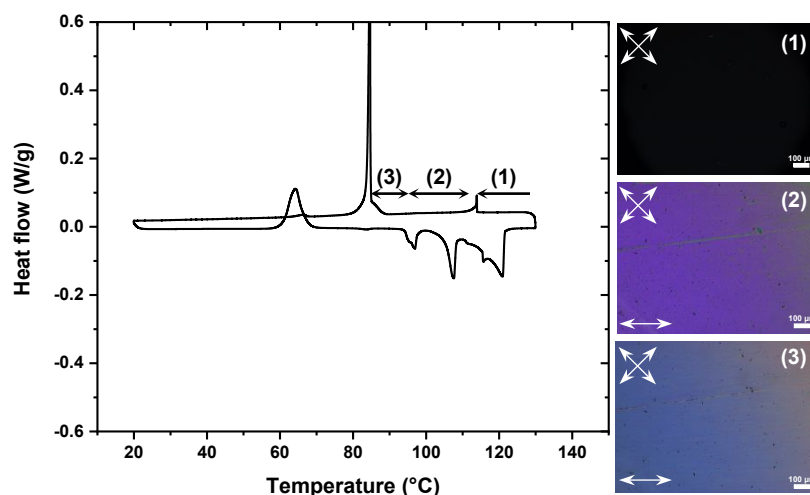


Figure S5: DSC measurement and POM images of a LC mixture with a M1/M2 composition of 70/30, a photoinitiator, and an inhibitor. Measurement was taken at a heating/cooling rate of 3 °C/minute (exothermal down). The POM images correspond to respectively isotropic (1), nematic (2), and smectic (3) phases in the DSC graph. The single arrow represents the alignment direction. The axis of the crossed polarizers are represented by the crossed arrows.

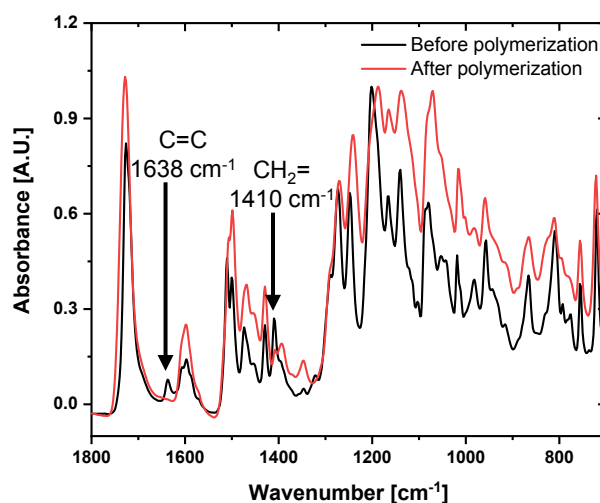


Figure S6: FT-IR analysis of an LC mixture (M1/M2 composition of 50/50) before and after polymerization.

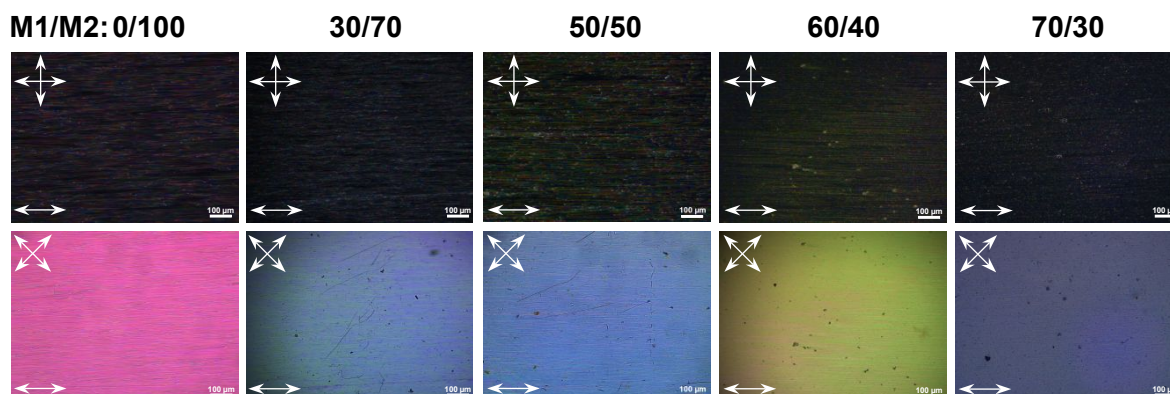


Figure S7: POM images of the polymerized LC membranes with various M1/M2 compositions. POM images show different birefringence caused by molecular order and orientation. The single arrow represents the alignment direction. The axes of the crossed polarizers are represented by the crossed arrows.

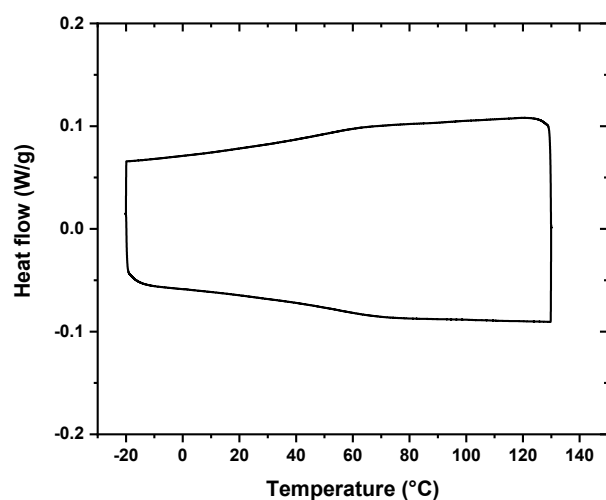


Figure S8: DSC measurement of a LC membrane with a M1/M2 composition of 0/100. Measurement was taken at a heating/cooling rate of 10 °C/minute (exothermal down).

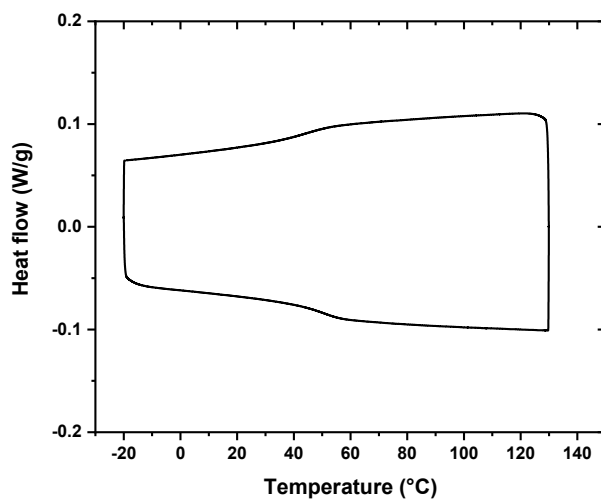


Figure S9: DSC measurement of a LC membrane with a M1/M2 composition of 30/70. Measurement was taken at a heating/cooling rate of 10 °C/minute (exothermal down).

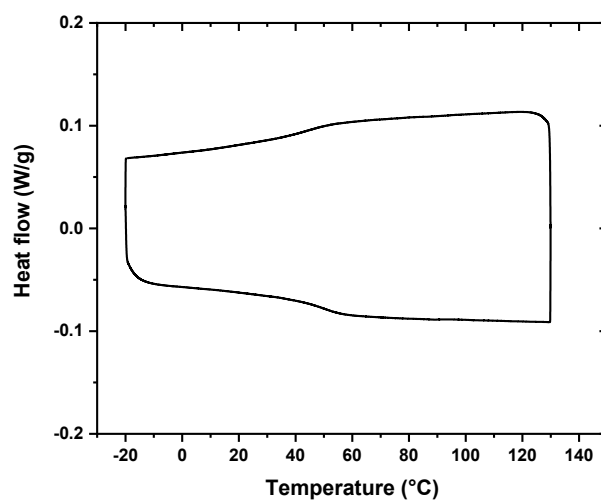


Figure S10: DSC measurement of a LC membrane with a M1/M2 composition of 50/50. Measurement was taken at a heating/cooling rate of 10 °C/minute (exothermal down).

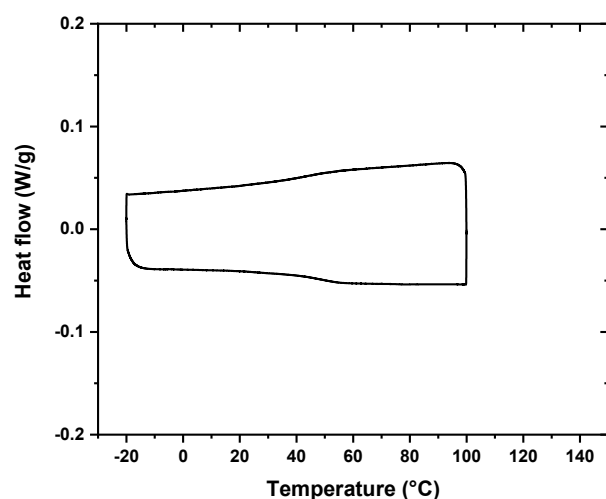


Figure S11: DSC measurement of a LC membrane with a M1/M2 composition of 60/40. Measurement was taken at a heating/cooling rate of 10 °C/minute (exothermal down).

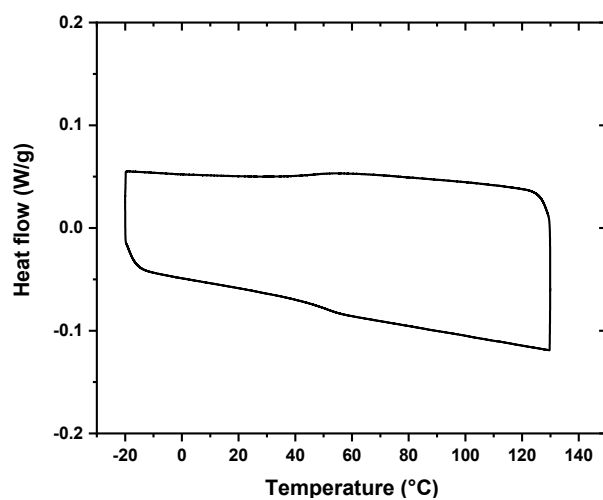


Figure S12: S11: DSC measurement of a LC membrane with a M1/M2 composition of 70/30. Measurement was taken at a heating/cooling rate of 10 °C/minute (exothermal down).

Table S1: Phase transition values of LC mixtures with different compositions of M1 and M2 determined from Figures S1–S5.

M1/M2	Isotropic [°C]	Nematic [°C]	Smectic C [°C]
0/100	>132	132-131	131-116
30/70	>121	121-116	116-107
50/50	>116	116-107	107-101
60/40	>115	115-103	103-95
70/30	>114	114-98	98-92

Table S2: Tilt, layer spacing, and intermolecular spacing of LC membranes with M1/M2 compositions of 0/100 and 70/30 measured at respectively 20 °C and 70 °C.

M1/M2	Temperature [°C]	Tilt angle [°]	Layer spacing [Å]	Intermolecular spacing [Å]
0/100	20	18	45.0	4.5
	70	19	44.8	4.5
	20	19	44.8	4.5
70/30	20	32	36.9	4.7
	70	31	37.1	4.7
	20	31	37.1	4.7

Table S3: Permeabilities (He, CO₂, Ar, and N₂) of LC membranes with various M1/M2 compositions at 20 °C and 6 bar feed pressure. The errors were calculated by taking the standard deviation of the permeability for the two independently measured membranes.

Permeability in Barrer [$10^{-10} \text{ (cm}^3 \cdot \text{cm) / (cm}^2 \cdot \text{s} \cdot \text{cmHg)}$] at 20 °C					
M1/M2	0/100	30/70	50/50	60/40	70/30
He	1.21 ± 0.01	1.17 ± 0.02	1.10 ± 0.03	1.05 ± 0.04	0.97 ± 0.03
CO ₂	0.34 ± 0.03	0.41 ± 0.02	0.37 ± 0.01	0.35 ± 0.02	0.33 ± 0.02
Ar	0.054 ± 0.002	0.058 ± 0.002	0.045 ± 0.002	0.041 ± 0.002	0.036 ± 0.002
N ₂	0.018 ± 0.001	0.018 ± 0.001	0.018 ± 0.001	0.014 ± 0.001	0.014 ± 0.001

Table S4: Ideal gas selectivities of LC membranes with various M1/M2 compositions at 20 °C and 6 bar feed pressure. The errors were calculated by taking the standard deviation of the ideal selectivity for the two independently measured membranes.

Ideal selectivity at 20 °C					
M1/M2	0/100	30/70	50/50	60/40	70/30
CO ₂ /N ₂	19.1 ± 0.9	22.0 ± 0.7	21.2 ± 0.6	21.9 ± 1.1	21.4 ± 0.2
He/N ₂	66.8 ± 0.2	64.6 ± 0.9	63.3 ± 1.8	65.1 ± 3.5	66.5 ± 1.1
He/CO ₂	3.5 ± 0.2	2.9 ± 0.1	3.0 ± 0.2	3.0 ± 0.1	3.1 ± 0.1
CO ₂ /Ar	6.4 ± 0.1	6.9 ± 0.1	8.4 ± 0.6	8.2 ± 0.1	8.6 ± 0.5

He/Ar	22.4 ± 0.9	20.3 ± 0.4	25.0 ± 0.5	24.3 ± 0.1	26.8 ± 1.0
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Table S5: Permeabilities (He, CO₂, Ar, and N₂) of LC membranes with various M1/M2 compositions at 40 °C and 6 bar feed pressure. The errors were calculated by taking the standard deviation of the permeability for the two independently measured membranes.

Permeability in Barrer [$10^{-10} (\text{cm}^3 \cdot \text{cm}) / (\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$] at 40 °C				
M1/M2	0/100	30/70	50/50	70/30
He	2.52 ± 0.05	2.37 ± 0.02	2.22 ± 0.03	2.09 ± 0.01
CO₂	0.86 ± 0.02	0.99 ± 0.01	0.90 ± 0.03	0.86 ± 0.01
Ar	0.172 ± 0.010	0.156 ± 0.002	0.133 ± 0.006	0.122 ± 0.001
N₂	0.065 ± 0.004	0.062 ± 0.001	0.056 ± 0.001	0.052 ± 0.001

Table S6: Ideal gas selectivities of LC membranes with various M1/M2 compositions at 40 °C and 6 bar feed pressure. The errors were calculated by taking the standard deviation of the ideal selectivity for the two independently measured membranes.

Ideal selectivity at 40 °C				
M1/M2	0/100	30/70	50/50	70/30
CO₂/N₂	13.3 ± 0.8	16.1 ± 0.1	16.2 ± 0.4	16.6 ± 0.1
He/N₂	39.0 ± 2.3	38.6 ± 0.2	40.0 ± 0.2	40.1 ± 0.2
He/CO₂	2.9 ± 0.1	2.4 ± 0.1	2.5 ± 0.1	2.4 ± 0.1
CO₂/Ar	5.0 ± 0.2	6.3 ± 0.1	6.9 ± 0.1	7.1 ± 0.1
He/Ar	14.6 ± 0.4	15.1 ± 0.1	16.9 ± 0.5	17.1 ± 0.2

Table S7: Permeabilities (He, CO₂, Ar, and N₂) of LC membranes with various M1/M2 compositions at 70 °C and 6 bar feed pressure. The errors were calculated by taking the standard deviation of the permeability for the two independently measured membranes.

Permeability in Barrer [$10^{-10} (\text{cm}^3 \cdot \text{cm}) / (\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$] at 70 °C				
M1/M2	0/100	30/70	50/50	70/30
He	6.28 ± 0.06	6.32 ± 0.04	6.14 ± 0.05	5.99 ± 0.06
CO₂	3.04 ± 0.09	3.66 ± 0.02	3.74 ± 0.02	3.91 ± 0.08
Ar	0.79 ± 0.031	0.76 ± 0.003	0.77 ± 0.013	0.68 ± 0.007

N₂	0.32 ± 0.002	0.32 ± 0.002	0.32 ± 0.001	0.30 ± 0.002
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Table S8: Ideal gas selectivities of LC membranes with various M1/M2 compositions at 70 °C and 6 bar feed pressure. The errors were calculated by taking the standard deviation of the ideal selectivity for the two independently measured membranes.

Ideal selectivity at 70 °C				
M1/M2	0/100	30/70	50/50	70/30
CO₂/N₂	9.4 ± 0.3	11.4 ± 0.1	11.8 ± 0.1	13.0 ± 0.2
He/N₂	19.6 ± 0.2	19.7 ± 0.1	19.4 ± 0.1	19.9 ± 0.1
He/CO₂	2.1 ± 0.1	1.7 ± 0.1	1.6 ± 0.1	1.5 ± 0.1
CO₂/Ar	3.8 ± 0.1	4.8 ± 0.1	4.9 ± 0.1	5.8 ± 0.1
He/Ar	8.0 ± 0.1	8.3 ± 0.1	8.0 ± 0.1	8.8 ± 0.1

Table S9: The kinetic diameter, critical temperature and quadrupole moment of various gas species.

Gas species	Kinetic diameter [nm]	Critical temperature [K]	Quadrupole moment [cm²] · 10⁴⁰
He	0.26	5.19	0.00
CO₂	0.33	304.13	-13.71
Ar	0.34	151.00	0.00
N₂	0.36	126.20	-4.91