PHYSICAL CHEMISTRY

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Chemical
Thermodynamics

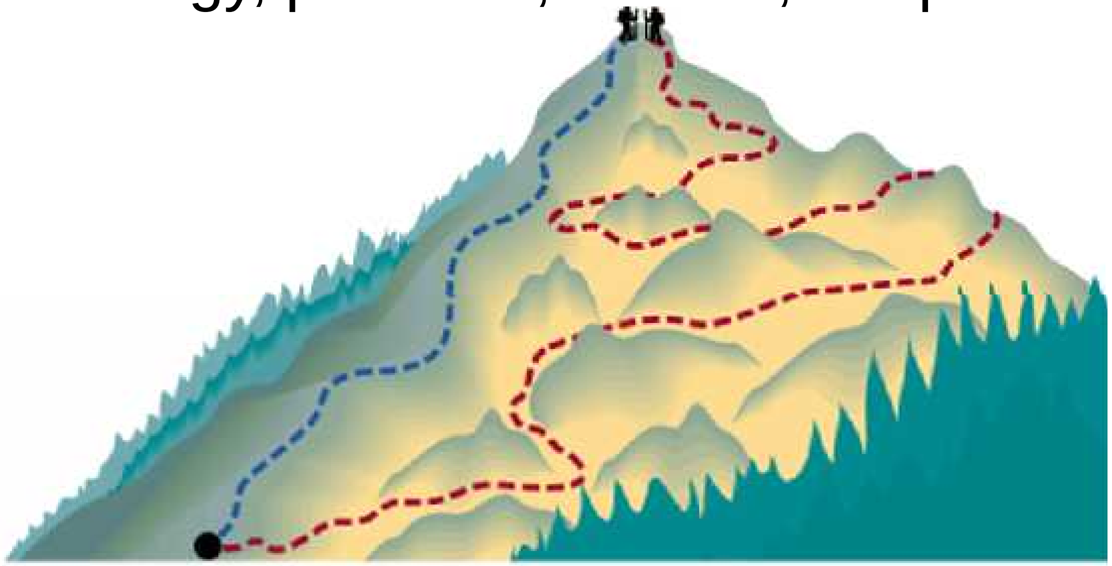
Law of Thermodynamics

1. The Zero Law of Thermodynamics
2. The First Law of Thermodynamics
3. The Second Law of Thermodynamics
4. The Third Law of Thermodynamics

Thermodynamics

State functions are properties that are determined by the state of the system, regardless of how that condition was achieved.

energy, pressure, volume, temperature



- Potential energy of hiker 1 and hiker 2 is the same even though they took different paths.
- Like total energy, E, and enthalpy, H, entropy is a state function. Therefore, $\Delta S = S_{final} - S_{initial}$

Entropi:

Ludwig Eduard Boltzmann (1844 – 1906) dengan konsep “zat terdiri atas partikel kecil yang bergerak acak” dan teori peluang:

Berkembang ke arah keadaan yang berpeluang lebih besar;

$$\boldsymbol{S = k \ln W}$$

k = Boltzmann constant (1.38×10^{-23} J/K)

The Second Law of Thermodynamics

The entropy of the universe does not change for reversible processes and increases for spontaneous processes.

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

Reversible (ideal):

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

Irreversible (real, spontaneous):

The entropy of the universe increases (real,spontaneous processes).

But, entropy can decrease for individual systems.

Entropy Changes in Surroundings

- Heat that flows into or out of the system also changes the entropy of the surroundings.
- For an isothermal process:

$$\Delta S_{surr} = \frac{-q_{sys}}{T}$$

  - At constant pressure, q_{sys} is simply $\Delta H°$ for the system.

$$\Delta S_{surr} = \frac{-q_{sys}}{T} = \frac{-\Delta H°}{T}$$

ENTROPY CHANGES SYSTEMS

1. Reversibly Processes

$T_{sys} = T_{surr}$

P, V dan T-nya.

$$S = q / T$$

$$q = q_{rev}$$

$$dS = dq_{rev}/T$$

$$\Delta S = q_{rev} / T$$

$$dS = dq/T$$

$$dq = dq_{rev}$$

Chemical Thermodynamics

Determaint Entropy Changes Reversibly Processes

1. Adiabatik Process, $dq = 0$

$dq_{rev} = 0$, and $dS = 0$ ➔ S

so➔ $dq_{rev} = 0$ and $dS = 0$

2. Isotermal Process ,

$PV = nRT$ and $dq = Cv.dT$

so

$$S_2 - S_1 = \int_1^2 \frac{d'Q_r}{T} = \frac{1}{T}\int_1^2 d'Q_r = \frac{Q_r}{T}$$

$$(s_2 - s_1)_v = \int_{T_1}^{T_2} c_v \frac{dT}{T}$$

$$(s_2 - s_1)_v = c_v \ln \frac{T_2}{T_1}$$

3. **Isotermal in the ideal Gas** $\Delta S = q_{rev} = nRT \ln V_2 / V_1$

2. **Proses Irreversibel**

$\Delta S_{univ} = \Delta S_{sis} + \Delta S_{surr}$

$\Delta S_{univ} \geq 0$

ΔS_{univ} -> $\Delta S_{sis} + \Delta S_{surr} \geq 0$

$\Delta S_{sis} \geq - \Delta S_{surr}$

$dS_{sis} \geq - dS_{surr}$

$dS_{sis} \geq dq/T$ Ketidaksamaan Clausius,

Chemical Thermodynamics

Proses Adiabatik $dq = 0$, tdk ada kalor yg dipindah

Hk 1…. $dU = dq + dW$

Pada pemuaian spontan gas tdk melakukkan kerja ($W = 0$)

$dU = dq$ -> pada V tetap dq_v

$C = q/T$ → $dq = C\,dT$ → C_p kapasitas panas pd P tetap

$dU = C\,dT$ → $dq_v = C_v\,dT$ → pada V tetap

$dq_p = C_p\,dT$ → pada P tetap

- $\Delta S = dq/T$ → $\Delta S = C_v \ln \frac{T_2}{T_1}$ dan $\Delta S = C_p \ln \frac{T_2}{T_1}$

Memperkirakan Nilai S^o Sistem

Berdasarkan pengamatan entropi zat akibat beberapa pengaruh keadaan :

1. Perubahan temperatur
2. Keadaan fisik dan perubahan fasa
3. Pelarutan solid atau liquid
4. Pelarutan gas
5. Ukuran atom atau kompleksitas molekul

1. Perubahan Temperatur

- S^o meningkat seiring dengan kenaikan temperatur

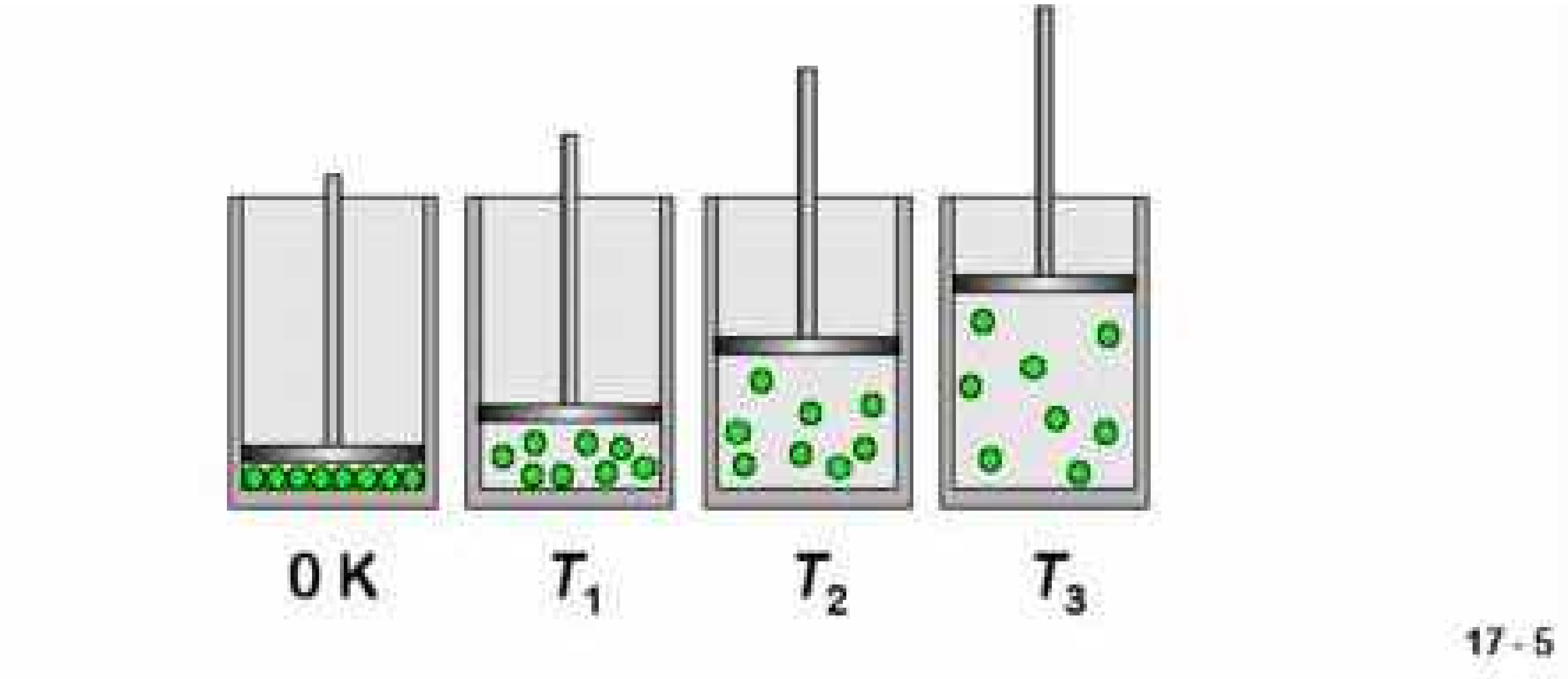
T(K)	273	295	298
S^o	31,0	32,9	33,1

- Kenaikan temperatur menunjukkan kenaikan energi kinetik rata-rata partikel

Entropi dan Temperatu

Entropi dari gas ideal pada tekanan tetap meningkat dengan meningkatnya temperatur

Hal ini karena volumenya bertambah



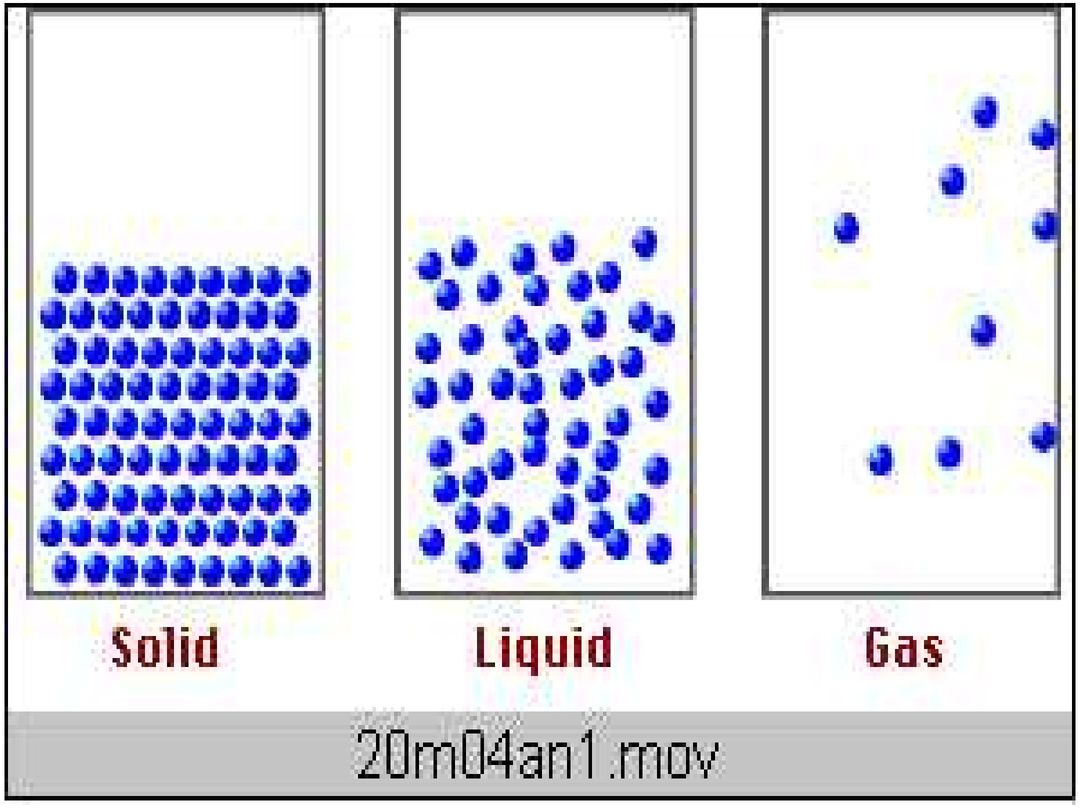
2. Keadaan Fisik dan Perubahan Fasa

- Ketika fasa yg lebih teratur berubah ke kurang teratur, perub entropi positif

- Entropi dalam sistem yang teratur kecil karena molekul-molekulnya hanya menempati posisi tertentu di dalam ruang.

  Teori Boltzmann : Entropi bertambah bila suatu zat padat mencair atau zat cair menguap dan akan turun bila transisi fasa terjadi dalam arah yang berlawanan.

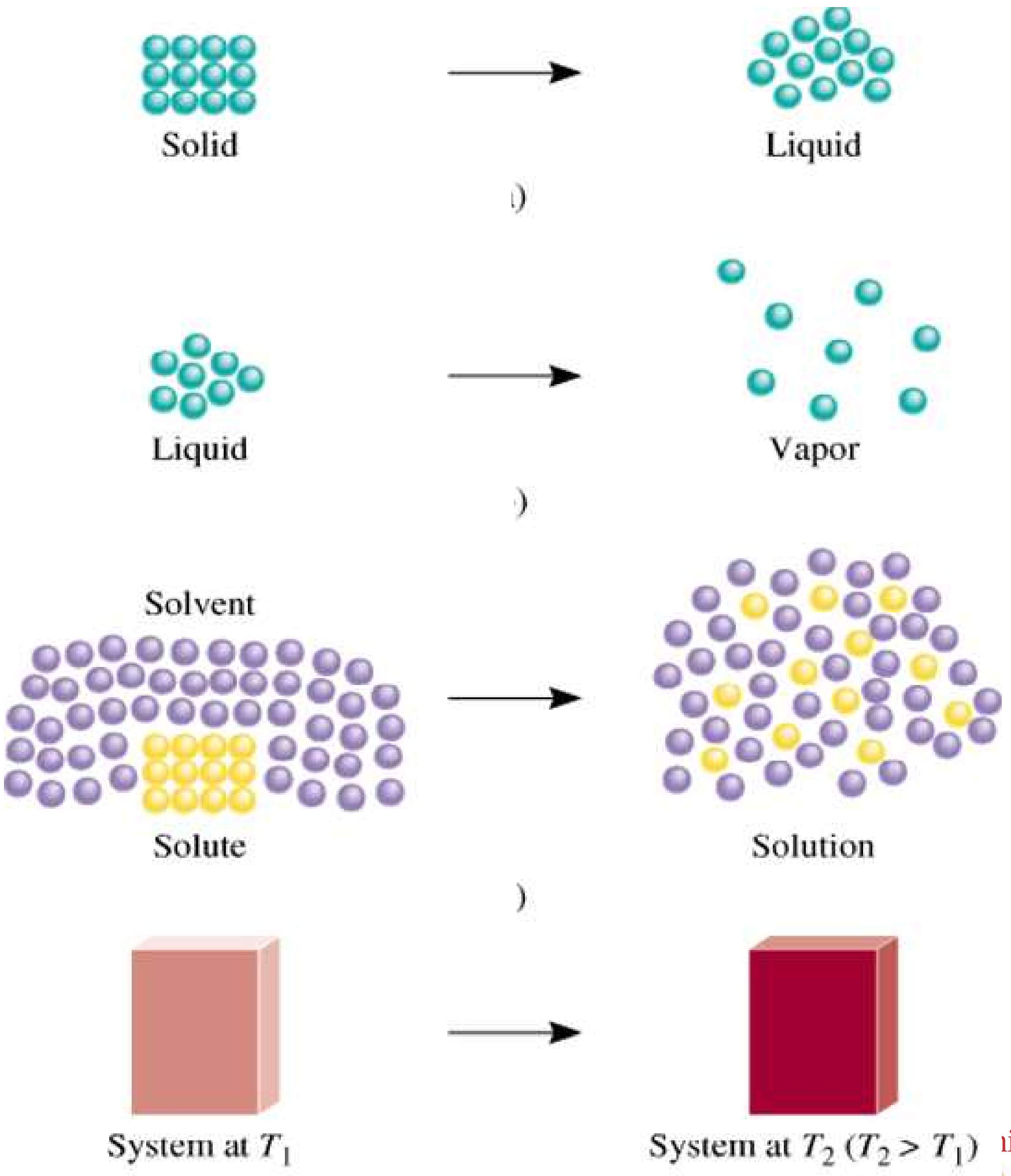
	Na	H_2O	C(grafit)
S^o (s / l)	51,4(s)	69,9 (l)	5,7(s)
S^o (g)	153,6	188,7	158,0



	S^o (J/K•mol)
H_2O(liq)	69.95
H_2O(gas)	188.8

S (gases) > S (liquids) > S (solids)

Proses yang menghasilkan kenaikan entropi ($S > 0$)



3. Pelarutan padatan atau cairan

- Entropi solid/liquid terlarut > larutan murni, jenis larutan dan pelarut

	NaCl	CH_3OH
S^o s/l	72.1(s)	127(l)
S^o aq	115,1	132

4. Pelarutan Gas

- Gas begitu tidak teratur dan akan jadi lebih teratur saat dilarutkan dlm larutan/ padatan

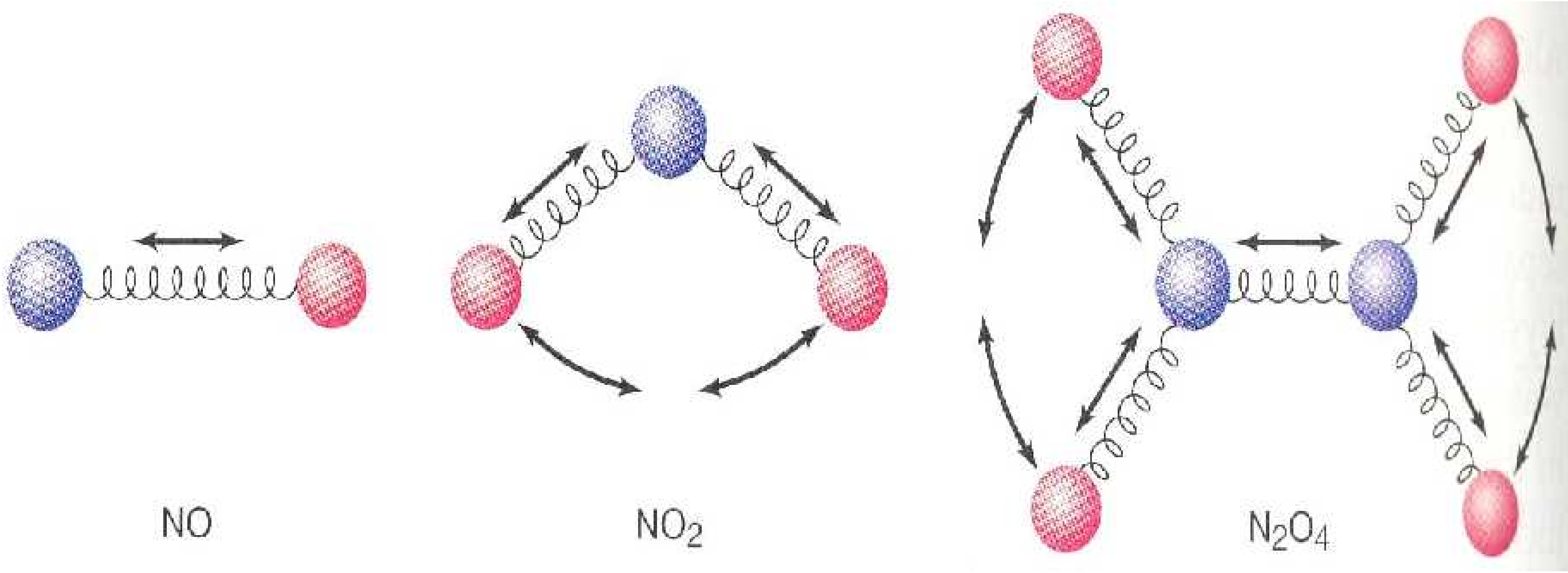
- Entropi larutan gas dlm larutan/ padatan
- selalu lebih kecil dibanding gas murni

- Saat O_2 (S^o g = 205,0J/mol K) dilarutkan dalam air, entropi turun drastis (S^o aq = 110,9 J/mol K)

5. Ukuran Atom Kompleksitas molekul

- Perbedaan entropi zat dg fasa sama tergantung ukuran atom dan kompleksitas molekul

	Li	Na	K	Rb	Cs
Jari2	152	186	227	248	265
M molar	6.941	22.99	39.10	85.47	132.9
$S^o(s)$	29.1	51.4	64.7	69.5	85.2



Rantai hidrokarbon panjang dapat berotasi dan bervibrasi dengan lebih banyak cara dibanding rantai pendek

	CH_4	C_2H_6	C_3H_8	C_4H_{10}
• S^o	186	230	270	310

Chemical Thermodynamics

Entropies

TABLE 18.2	Standard Entropy Values ($S°$) for Some Substances at 25°C		
Substance	**$S°$ (J/K · mol)**	**Substance**	**$S°$ (J/K · mol)**
$H_2O(l)$	69.9	C(diamond)	2.4
$H_2O(g)$	188.7	C(graphite)	5.69
$Br_2(l)$	152.3	$CH_4(g)$ (methane)	186.2
$Br_2(g)$	245.3	$C_2H_4(g)$ (ethane)	229.5
$I_2(s)$	116.7	He(g)	126.1
$I_2(g)$	260.6	Ne(g)	146.2

THANK YOU

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