ChemE 2200 – Chemical Thermodynamics Lecture 5

Today:

- 2nd Law of Thermodynamics: $\Delta S > 0$ for spontaneous processes.
- Calculating Entropy Changes for Isolated Systems:
  - Heat flow from hot to cold.
  - Gas expansion from high pressure to low pressure.
  - Gases mixing.
  - Vaporization.
- Entropy and Statistical Probability.

Defining Question:

What famous equation relates entropy to statistical probability?

Reading for Today's Lecture:

McQuarrie & Simon, Chapter 20.4–20.6

Reading for Thermodynamics Lecture 6:

McQuarrie & Simon, Chapter 20.7.

1st Prelim

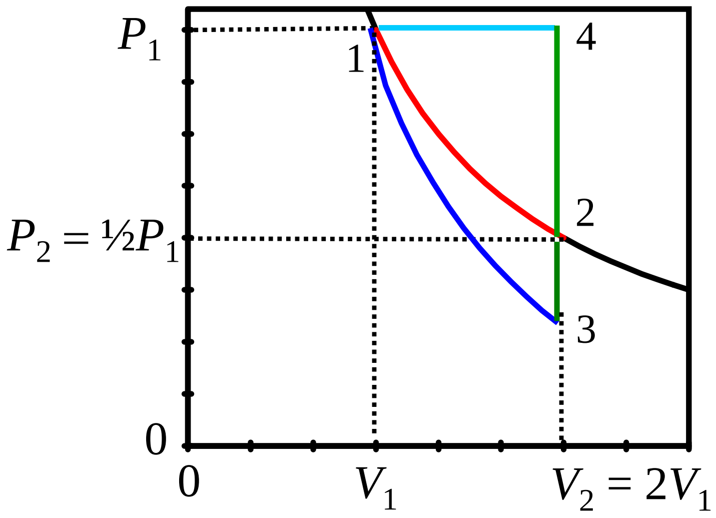
Tuesday, March 11, 7:30 – 9:30 p.m.

245 Olin Hall

Covers –
- Atomic Orbitals
- Molecular Orbitals
- Atomic and Molecular Spectroscopy
- Electrons in Solids
- Classical Thermodynamics through 1st Law

Covers –
- Lectures through 1st half of Monday, 2/24 (Lecture T4)
- Homework through Homework 5
- Calculation Sessions through Calculation Session 5

You may use a hand-written, double-sided reference sheet.
Reference sheets will be submitted with the Prelim.
Reference sheets will be returned Wednesday, March 12.



Recap

Isothermal, $\Delta T = 0$

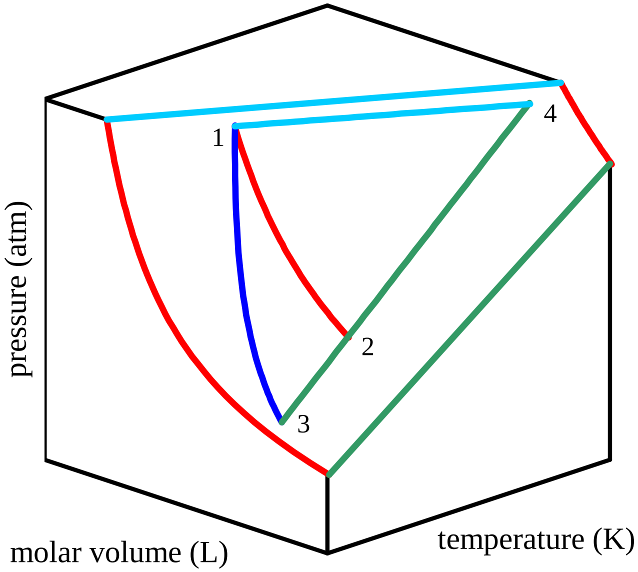
Adiabatic, $q = 0$

Isochoric, $\Delta V = 0$

Isobaric, $\Delta P = 0$

$T_1 = T_2$, $P_1 = P_4$

$V_2 = V_3 = V_4$

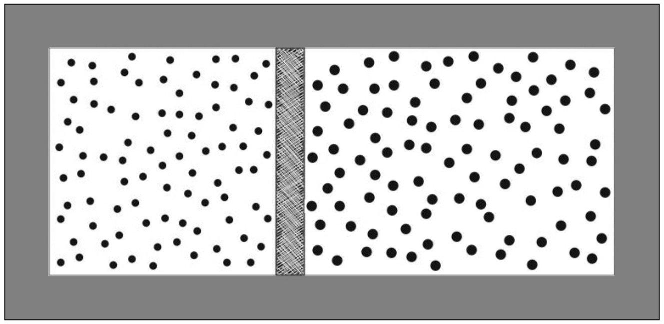


path	type	heat, q_{rev}	$\Delta S = \int \frac{\delta q_{\text{rev}}}{T}$	
$1 \rightarrow 2$	isothermal	$nRT \ln \frac{V_2}{V_1}$	$nR \ln \frac{V_2}{V_1}$	
$1 \rightarrow 3$	adiabatic	0	0	$\Delta S = nR \ln \frac{V_2}{V_1}$
$3 \rightarrow 2$	isochoric	$\int_{T_3}^{T_2} C_V dT$	$\int_{T_3}^{T_2} \frac{\overline{C}_V}{T} dT = nR \ln \frac{V_2}{V_1}$	
$1 \rightarrow 4$	isobaric	$\int_{T_1}^{T_4} C_V dT + P_1(V_2 - V_1)$	$\int_{T_1}^{T_4} \frac{C_V}{T} dT + nR \ln \frac{V_2}{V_1}$	$\Delta S = nR \ln \frac{V_2}{V_1}$
$4 \rightarrow 2$	isochoric	$-\int_{T_1}^{T_4} C_V dT$	$-\int_{T_1}^{T_4} \frac{C_V}{T} dT$	

The Second Law of Thermodynamics

Spontaneous processes require $\Delta S > 0$.

Consider two gases separated by a fixed impermeable barrier, but isolated from surroundings.



Gas A
P_A, T_A, V_A

Gas B
P_B, T_B, V_B

Example in McQuarrie & Simon, Section 20.4: $\underline{V_A \text{ and } V_B \text{ fixed}}$, $T_A \neq T_B$

Useful equation: $\delta q_{\text{rev}} = dU - \delta w_{\text{rev}}$

$$TdS = dU + \cancelto{0}{PdV}$$

$$dS = \frac{dU}{T}$$ constant volume

System is isolated, so $U_{\text{total}} = U_A + U_B = \text{constant}$

$$dU_{\text{total}} = dU_A + dU_B = 0$$

$$dU_A = -dU_B$$

$$dS_{\text{total}} = dS_A + dS_B$$

$$dS_{\text{total}} = \frac{dU_A}{T_A} + \frac{dU_B}{T_B}$$

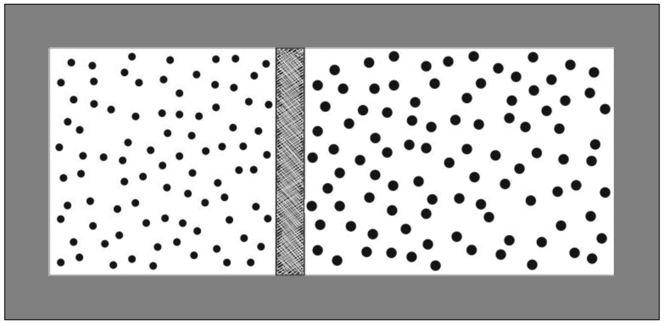
$$dS_{\text{total}} = \frac{dU_A}{T_A} - \frac{dU_A}{T_B}$$

$$\boxed{dS_{\text{total}} = \left(\frac{1}{T_A} - \frac{1}{T_B}\right)dU_A}$$

The Second Law of Thermodynamics

Spontaneous processes require $\Delta S > 0$.

Consider two gases separated by a fixed heat-conducting barrier, but isolated from surroundings.



Gas A
P_A, T_A, V_A

Gas B
P_B, T_B, V_B

Example in McQuarrie & Simon, Section 20.4: V_A and V_B fixed, $T_A \neq T_B$

From previous slide,

$$\boxed{dS_{\text{total}} = \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU_A}$$

Assume $T_B > T_A$ Thus $\frac{1}{T_A} > \frac{1}{T_B}$, $\left(\frac{1}{T_A} - \frac{1}{T_B}\right) > 0$

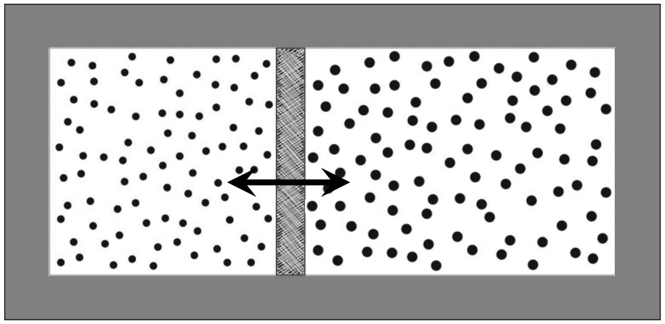
If heat flows from hot Gas B to cold Gas A, $dU_A > 0$ $\Rightarrow$ $dS_{\text{total}} > 0$.

~~If heat flows from cold Gas A to hot Gas B, $dU_A < 0$ $\Rightarrow$ $dS_{\text{total}} < 0$.~~

$\therefore$ heat flows from hot (T_B) to cold (T_A).

The Second Law of Thermodynamics

New example: Consider two gases separated by a *movable* barrier, but isolated from surroundings.



$T_A = T_B,\ P_A \neq P_B$

Gas A
P_A, T_A, V_A

Gas B
P_B, T_B, V_B

Useful equation: $\delta q_{rev} = dU - \delta w_{rev}$

$$TdS = dU + PdV$$

$$dS = \frac{dU}{T} + \frac{P}{T}dV$$

System is isolated, so $dU_A = -dU_B$ as before

Total volume is fixed, so

$$V_{total} = V_A + V_B = \text{constant}$$

$$dV_{total} = dV_A + dV_B = 0$$

$$dV_A = -dV_B$$

$$dS_{total} = dS_A + dS_B$$

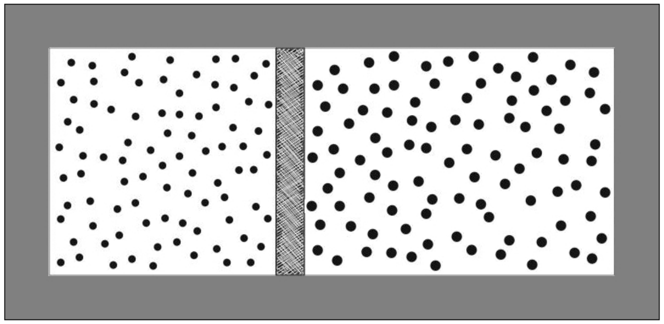
$$dS_{total} = \left(\frac{dU_A}{T_A} + \frac{P_A}{T_A}dV_A\right) + \left(\frac{dU_B}{T_B} + \frac{P_B}{T_B}dV_B\right)$$

$$dS_{total} = \left(\frac{dU_A}{T_A} + \frac{P_A}{T_A}dV_A\right) + \left(\frac{-dU_A}{T_B} - \frac{P_B}{T_B}dV_A\right)$$

$$dS_{total} = \cancelto{0}{\left(\frac{1}{T_A} - \frac{1}{T_B}\right)}dU_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right)dV_A \quad \boxed{= \frac{1}{T_A}\left(P_A - P_B\right)dV_A}$$

The Second Law of Thermodynamics

Consider two gases separated by a *movable* barrier, but isolated from surroundings.



New Example: $T_A = T_B$, $P_A \neq P_B$

Gas A
P_A, T_A, V_A

Gas B
P_B, T_B, V_B

$$\boxed{dS_{\text{total}} = \frac{1}{T_A}\left(P_A - P_B\right)dV_A}$$

Assume $P_B > P_A$ thus $(P_A - P_B) < 0$

If higher pressure Gas B expands, $dV_A < 0$, $\Rightarrow$ $dS_{\text{total}} > 0$.

~~If lower pressure Gas A expands, $dV_A > 0$, $\Rightarrow$ $dS_{\text{total}} < 0$.~~

$\therefore$ higher-pressure gas expands, lower-pressure gas compresses.

Summary of Thermodynamics to date

For an isolated system, $\Delta U_{\text{system}} = 0$, $\underline{\Delta S_{\text{system}} > 0}$

2nd Law of Thermodynamics.

Entropy is not conserved.

$$dS = \frac{\delta q_{\text{rev}}}{T} \qquad dS \geq \frac{\delta q}{T} \qquad \Delta S \geq \int \frac{\delta q}{T}$$

For a cyclic process, $\Delta U_{\text{system}} = 0$, $\Delta H_{\text{system}} = 0$, $\Delta S_{\text{system}} = 0$

Internal Energy, Enthalpy, and Entropy are State Functions

For a cyclic process, $\Delta U_{\text{surroundings}} = 0$, $\Delta H_{\text{surroundings}} = 0$, $\Delta S_{\text{surroundings}} > 0$

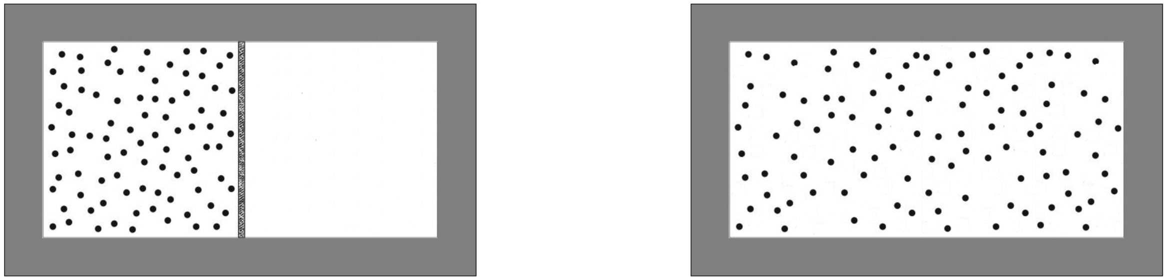
Total energy of the universe is conserved,
but entropy increases.

Entropy and Statistical Probability

McQuarrie & Simon: deductive explanation ⇒ general equations

Consider an inductive explanation ⇒ specific equations

ideal gas,
adiabatic system



before

after

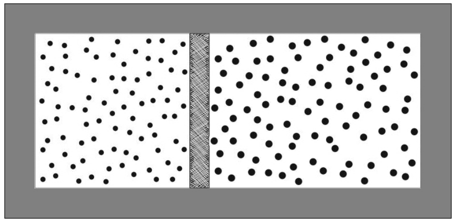
ideal gas expands into a vacuum: $q = 0$, $w = 0$ ⇒ $\Delta U = 0$, $\Delta T = 0$

# of molecules in the system	probability that the molecules are in the box	probability that the molecules are in the left side of the box
1	1	½
2	1	$(½)^2$
3	1	$(½)^3$
⋮	⋮	⋮
N_A	1	$(½)^N$

Entropy and Statistical Probability

Ludwig Boltzmann postulated (1872) $S = k \ln\Omega$ from his Kinetic Theory of Gases

such that $\Omega \equiv$ number of equally probable states.



Gas A Gas B

$S_{\text{total}} = S_A + S_B$ *S* is additive

If $S \propto \Omega$, total number of states $= \Omega_A \cdot \Omega_B$, $S_{\text{total}} \propto S_A \cdot S_B$ *S* is not additive if $S \propto \Omega$

But for $S_A = k \ln\Omega_A$, $S_B = k \ln\Omega_B$

$$S_{\text{total}} = k \ln(\Omega_A \cdot \Omega_B) = k \ln\Omega_A + k \ln\Omega_B = S_A + S_B$$ *S* is additive!

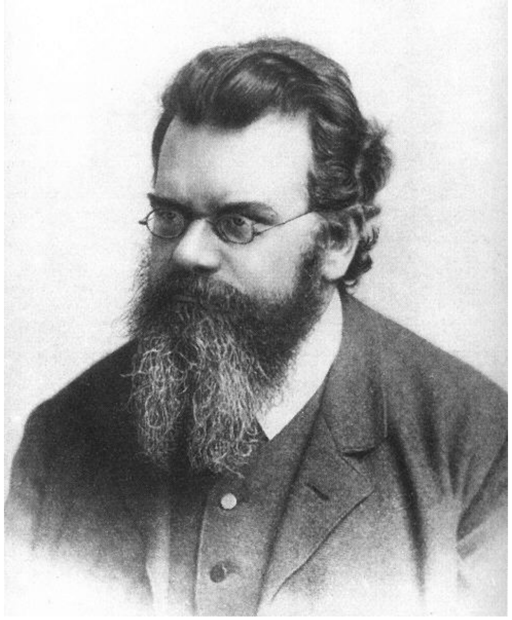
For expansion into a vacuum, $\Delta S = S_{\text{after}} - S_{\text{before}} = k \ln[1 \times N_{\text{states}}] - k \ln[(½)^N \times N_{\text{states}}]$

$$= k \ln \frac{N_{\text{states}}}{(½)^{N_A} N_{\text{states}}} = k \ln[(2)^{N_A}] = k N_A \ln 2$$

$$\Delta S = R \ln 2$$

$\Delta S > 0$ expansion into a vacuum is spontaneous

Ludwig Boltzmann (1844-1906)



Boltzmann lecturing
©University of Vienna

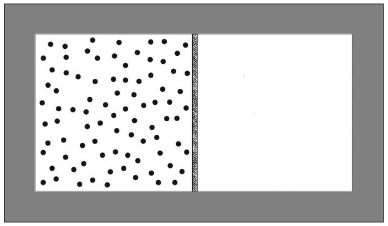
Known for

- Boltzmann constant, k
- Boltzmann equation, $S = k \ln\Omega$
- Boltzmann distribution
- Detailed balance for chemical equilibrium
- H-theorem; aka 2nd Law of Thermodynamics
- Maxwell–Boltzmann statistics
- Stefan–Boltzmann constant, σ
- Stefan–Boltzmann law, $j = \sigma T^4$
- Epistemological idealism

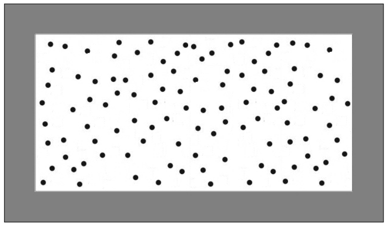
All knowledge is based on the mind's ideas.

Must Devise a *Reversible* Path between Two States to Calculate ΔS

ideal gas,
adiabatic system



before



after

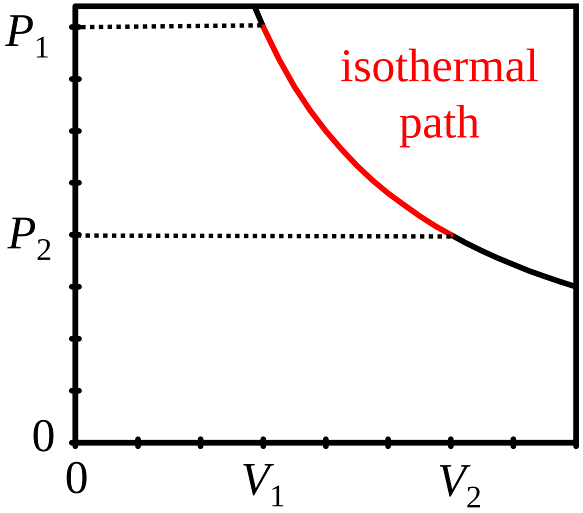
From molecular probability,
$\Delta S = R \ln 2$

1st Law Analysis: ideal gas expands into a vacuum: $q = 0$, $w = 0 \quad \Rightarrow \quad \Delta U = 0, \Delta T = 0$

2nd Law Analysis: $\Delta S = \int \frac{\delta q_{\mathrm{rev}}}{T} = \int \frac{0}{T} = 0$ Error? $q \neq q_{\mathrm{rev}}$

Must devise a *reversible* path between initial and final states.

How to expand a gas such that $T_{\mathrm{final}} = T_{\mathrm{initial}}$? $\Delta U = 0 = q_{\mathrm{rev}} + w_{\mathrm{rev}}$

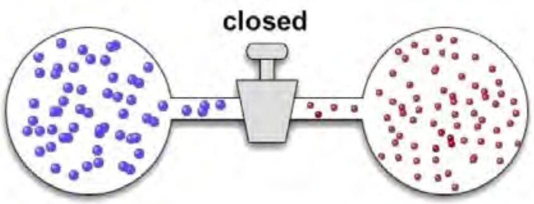


$$\delta w_{\mathrm{rev}} = -P dV = -\frac{nRT}{V} dV$$

$$\delta q_{\mathrm{rev}} = -\delta w_{\mathrm{rev}} = \frac{nRT}{V} dV$$

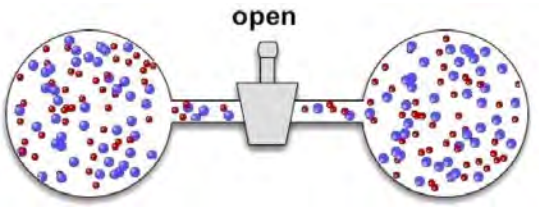
$$\Delta S = \int \frac{\delta q_{\mathrm{rev}}}{T} = nR \int_{V_1}^{2V_1} \frac{dV}{V} = nR \ln \frac{2V_1}{V_1} = R \ln 2$$ ✓

Entropy of Mixing (Example 20-3 in McQuarrie & Simon)



Gas A
N_A mols

Gas B
N_B mols



ideal gases,
$P_A = P_B,\ T_A = T_B$

image: http://umdberg.pbworks.com

$$\text{Given}:\ \Omega \propto \left(\frac{8ma^2E}{h^2}\right)^{3N/2} \propto E^{3N/2}(a^2)^{3N/2} \propto E^{3N/2}(a^3)^N \propto E^{3N/2}V^N$$

exercise 20-23

$$\Delta S_{\text{mixing}} = S_{\text{mixture}} - (S_A + S_B) = k\ln\Omega_{\text{mixture}} - (k\ln\Omega_A + k\ln\Omega_B) = k\ln\frac{\Omega_{\text{mixture}}}{\Omega_A\Omega_B}$$

$$= k\ln\frac{\cancel{E_A^{3N/2}}(V_A+V_B)^{N_A}\times\cancel{E_B^{3N/2}}(V_A+V_B)^{N_B}}{\cancel{E_A^{3N/2}}(V_A)^{N_A}\times\cancel{E_B^{3N/2}}(V_B)^{N_B}} = k\ln\left(\frac{V_A+V_B}{V_A}\right)^{N_A}\left(\frac{V_A+V_B}{V_B}\right)^{N_B}$$

$$= kN_A\ln\left(\frac{N_A+N_B}{N_A}\right) + kN_B\ln\left(\frac{N_A+N_B}{N_B}\right)$$

At constant pressure, $n \propto V$

$$= -kN_A\ln\left(\frac{N_A}{N_A+N_B}\right) - kN_B\ln\left(\frac{N_A}{N_A+N_B}\right)$$

define $y_A = \dfrac{N_A}{N_A+N_B}$

divide by $(N_A + N_B)$

note: molar

$$\Delta\overline{S}_{\text{mixing}} = -y_AR\ln(y_A) - y_BR\ln(y_B) > 0$$

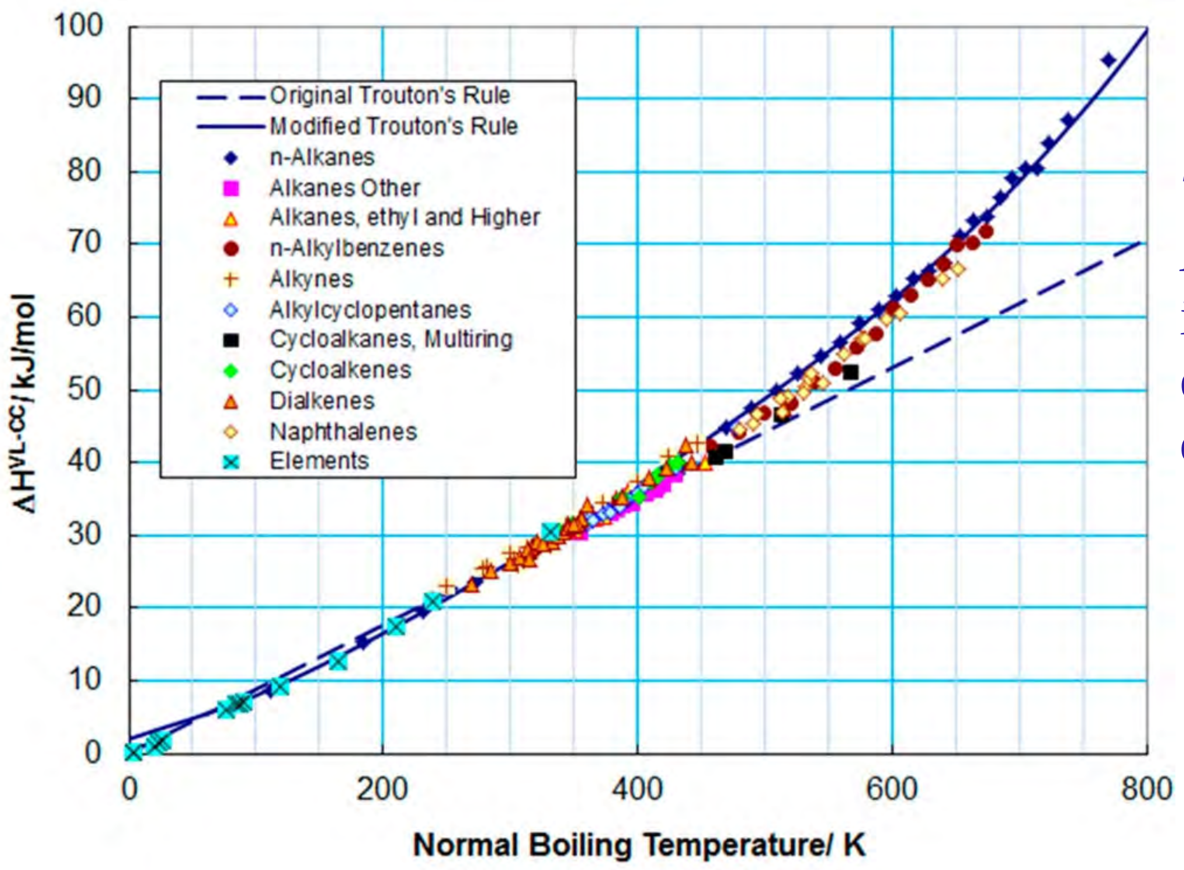
eqn (20.30, p. 836)

Entropy of Vaporization

n-hexane: b.p. = 68.7C at 1 atm, $\Delta H_{\text{vaporization}}$ = 28.85 kJ/mol

$$\Delta S_{\text{vaporization}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta H_{\text{vaporization}}}{T} = \frac{28.85\ \text{kJ/mol}}{341.8\text{K}} = 84.4\ \text{J/(K}\cdot\text{mol)}$$

$\Delta S_{\text{vaporization}}$ ≈ 85-88 J/(K·mol) ≈ 10.5R for most molecular liquids *Trouton's Rule* (1884)



The modified Trouton's Rule Includes intermolecular effects, such as dipolar attraction.

Modified Trouton's Rule for the Estimation, Correlation, and Evaluation of Pure-Component Vapor Pressure,
P. M. Mathias, G. Jacobs, and J. Cabrera, J. Chem. Eng. Data, **63**, 943-953 (2018).

To calculate ΔS, one must devise
a *reversible* path between two states