

Enthalpy and Entropy



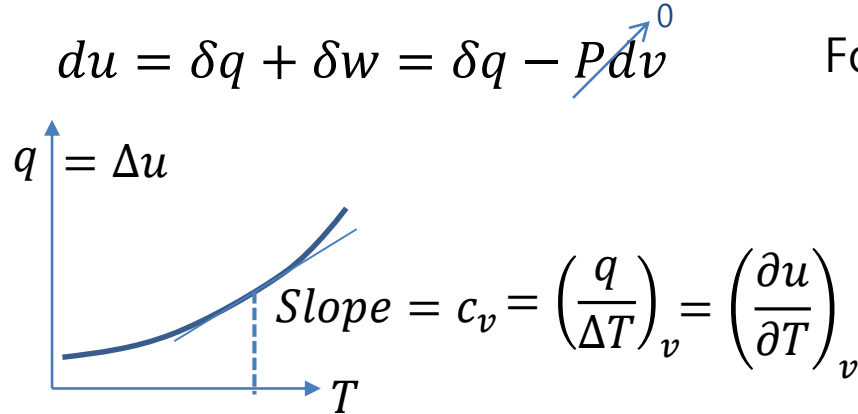
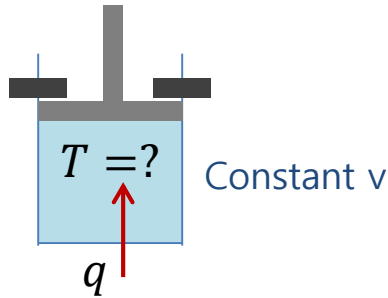
How to know $\Delta u, \Delta h$?

- u and h is not measurable directly.
- u and h is associated with heat capacity
- The heat capacity is measurable from experiment!

Heat Capacity	Specific heat capacity	Molar heat capacity
$C = Q/\Delta T$	$c = q/\Delta T$	$c = q/\Delta T$
Extensive Property	Intensive Property	Intensive Property
J/K	J/K·g (cal/g·K)	J/K·mol

Heat Capacity and U, H

c_v



For ideal gas, $u=f(T)$ only

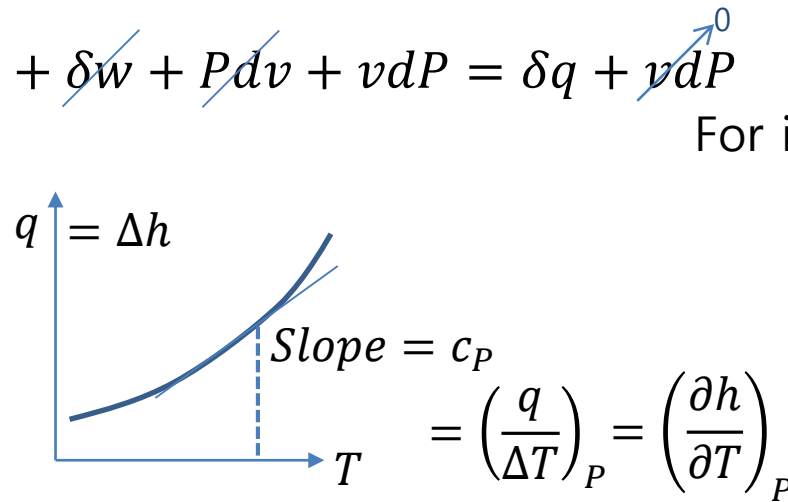
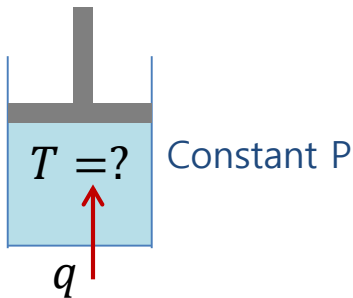
$$c_v = \left(\frac{\partial u}{\partial T} \right)_v = \frac{du}{dT}$$

$$du = c_v dT$$

$$\Delta u = \int c_v dT$$

c_p

$$dh = d(u + Pv) = \delta q + \cancel{\delta w} + Pdv + vdP = \delta q + v dP$$



For ideal gas, $h=u+Pv=u+RT$
 $h=f(T)$ only

$$c_p = \left(\frac{\partial h}{\partial T} \right)_P = \frac{dh}{dT}$$

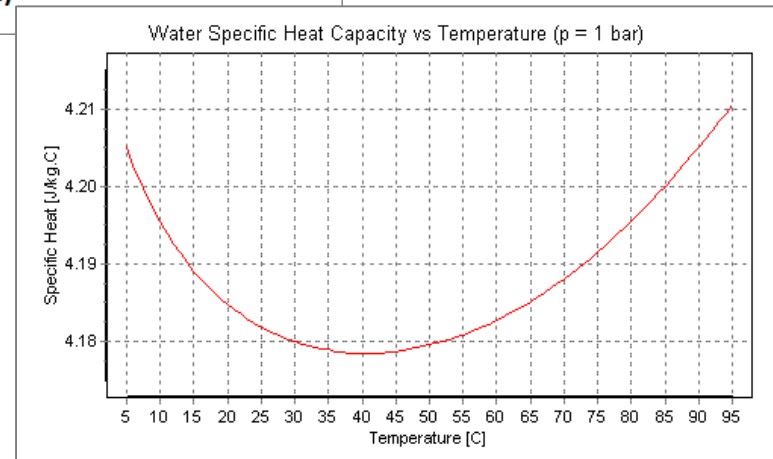
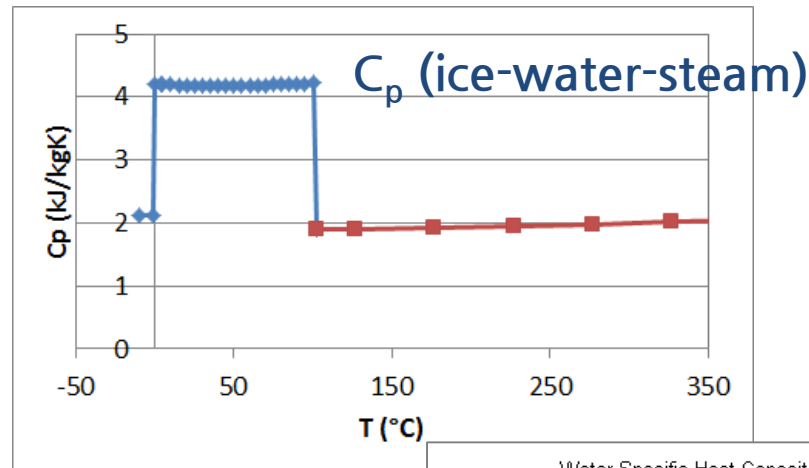
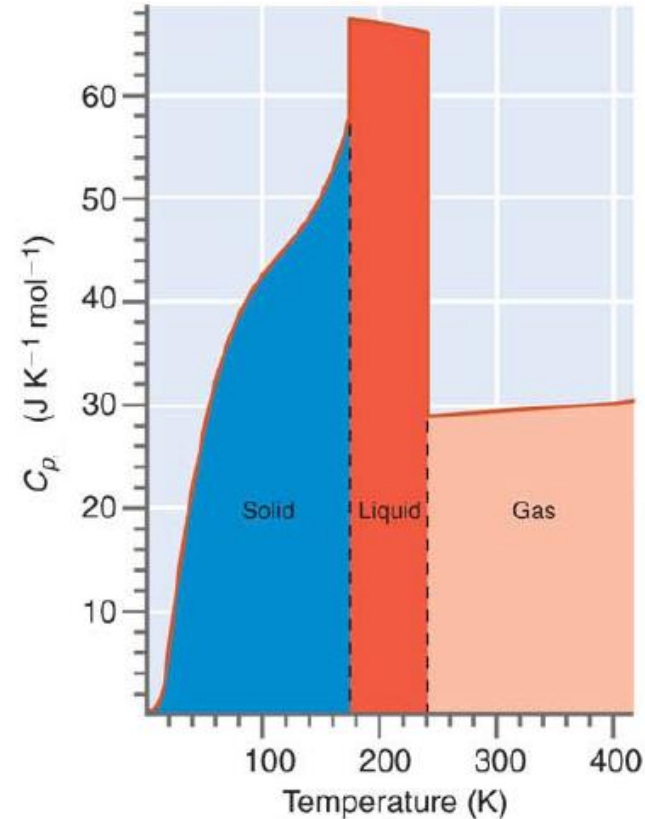
$$dh = c_p dT$$

$$\Delta h = \int c_p dT$$

Correlation for Δh from experiment

$$\frac{C_P}{R} = A + BT + CT^2 + DT^{-2} + ET^3 [K]$$

(Ideal gas condition) \rightarrow good approximation with at low P



c_p and c_v

- For solids and liquids

- $c_p \approx c_v$

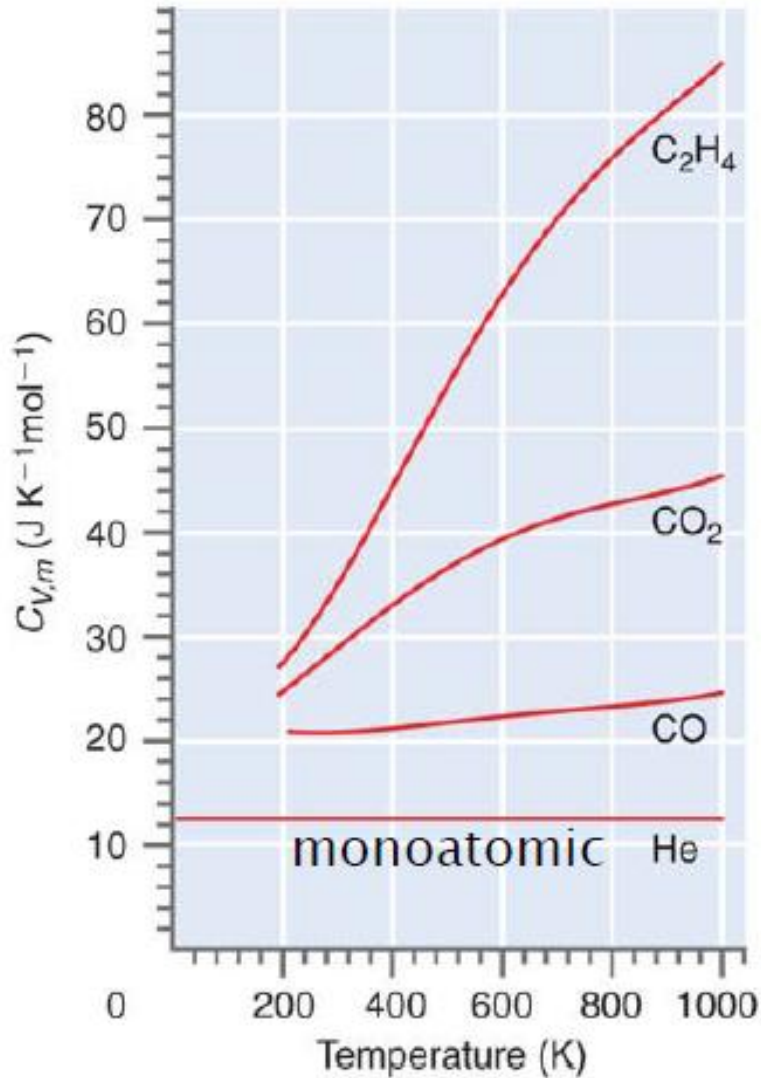
$$c_p \equiv \left(\frac{\partial h}{\partial T} \right)_P = \left(\frac{\partial(u + Pv)}{\partial T} \right)_P = \left(\frac{\partial u}{\partial T} \right)_P + \left(\frac{\partial RT}{\partial T} \right)_P = \left(\frac{\partial u}{\partial T} \right)_P + R$$

- For ideal gas,

$$\left(\frac{\partial u}{\partial T} \right)_P = \frac{du}{dT} = \left(\frac{\partial u}{\partial T} \right)_v$$

$$c_p = c_v + R$$

c_v of Gases

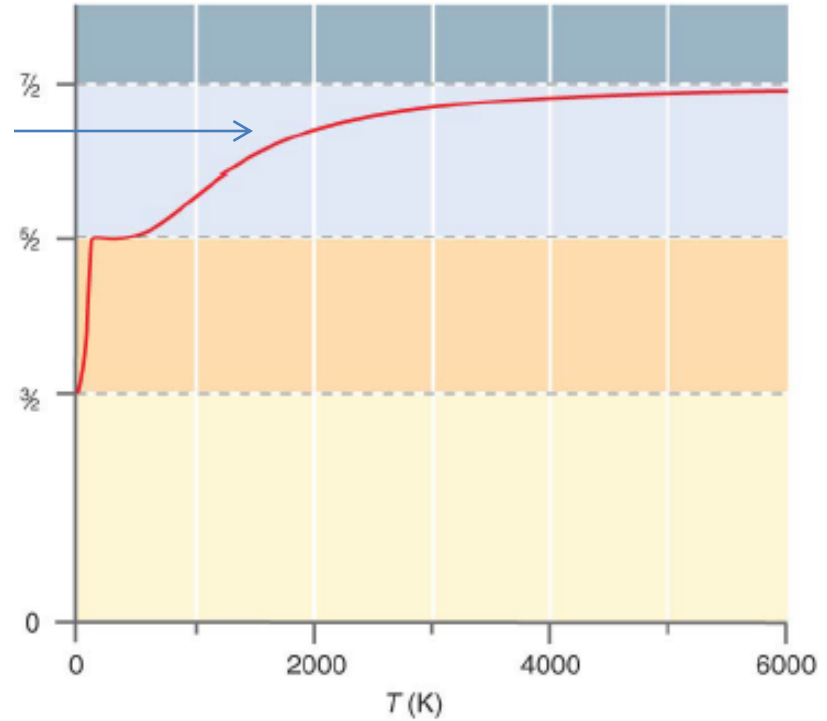


Polyatomic
 $c_v \approx 6/2 R + f(T)$

Linear
 $c_v \approx 5/2 R + f(T)$

Diatomic
 $c_v \approx 5/2 R$

$c_v \approx 3/2 R$

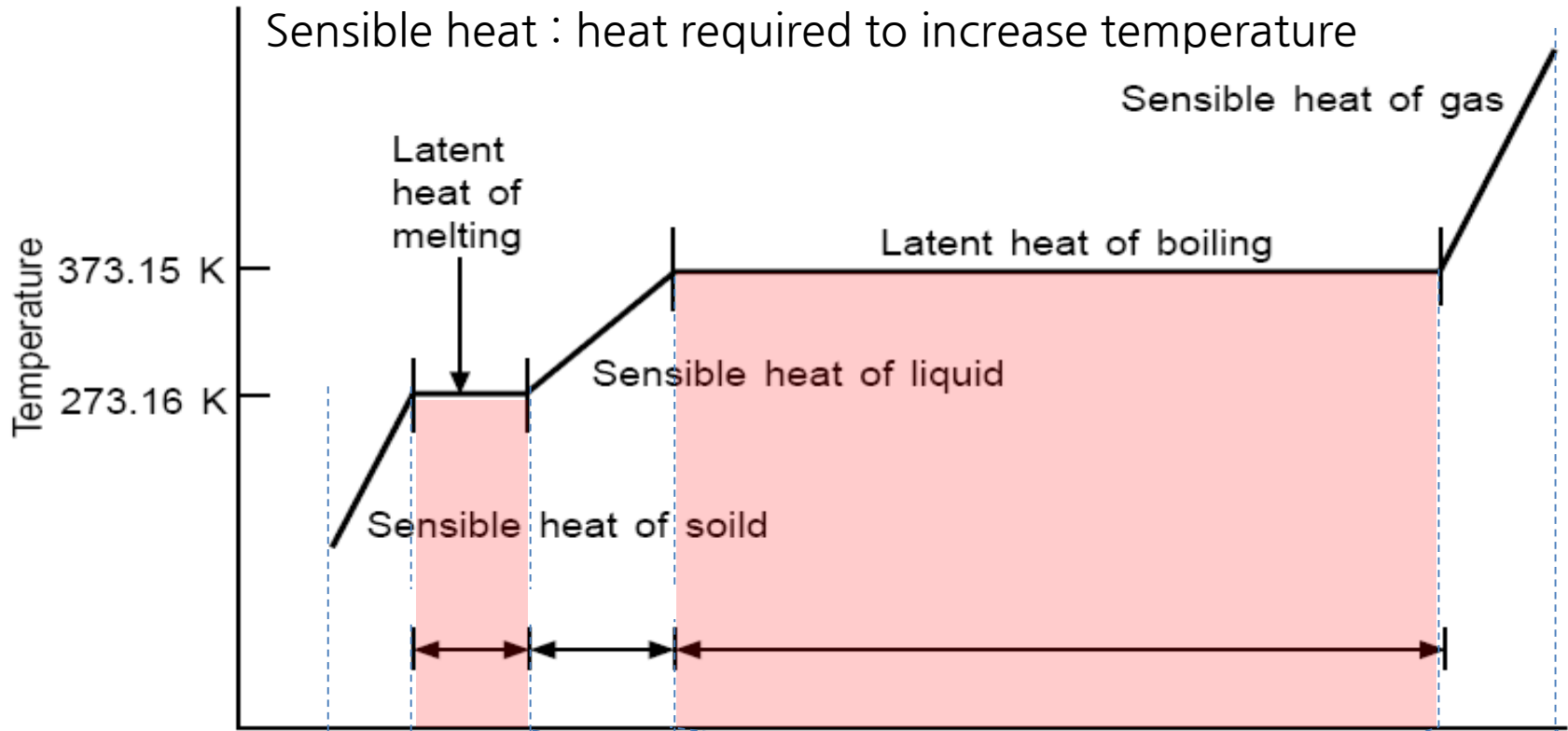


For an ideal gas,
 $c_v = 3/2 R$

Δh with Phase change

Latent heat : heat required to change the phase

Sensible heat : heat required to increase temperature



$$\Delta h = \int c_p dT = \int_{T_1}^{T_m} c_{p,solid} dT + \Delta h_{fus} + \int_{T_m}^{T_b} c_{p,liq} dT + \Delta h_{vap} + \int_{T_b}^{T_2} c_{p,gas} dT$$

Enthalpy of reaction

- **Standard enthalpy of formation, Δh_f^0**
 - Change of enthalpy when one mole of substance is formed from its pure element in nature at standard condition, 25°C, 1 atm
- **Standard enthalpy of reaction, Δh_{rxn}^0**
 - Change of enthalpy by a chemical reaction
 - $\Delta h_{rxn}^0 < 0$: exothermic reaction
 - $\Delta h_{rxn}^0 > 0$: endothermic reaction

Example 2.11

- In: 10 mol/s of hexane @25°C
- Out: 100°C vapor
- Q=? (435 kJ/s in the textbook)

18PR							

Example 2.15

- Propane in an adiabatic chamber at 25°C.
- (a) React with stoichiometric amount of oxygen
(T=4910K in textbook)

18PR	18PR	18SRK					
			3557				

- (b) React with stoichiometric amount of air
(T=2370K in textbook)

18PR							

- (c) React with stoichiometric amount of air and the product contains 90% CO₂ and 10% CO
(T=2350K in textbook)

18PR							

HHV vs LHV?



Understanding of Entropy, S

- **Difficult to understand the concept.**
 - Think about Enthalpy
 - H is hard to understand, because it is close to the mathematical notion, not natural discovery such as T or P.
 - Same for Entropy!
 - It was born as a notion, and cannot be explained clearly until 19th century.
 - It can be defined by two kinds of view:
 - The classical thermodynamics definition
 - The statistical mechanics definition.

Statistical understanding of S

- S is a measure of the number of possible configurations (Ω) of the individual molecules.

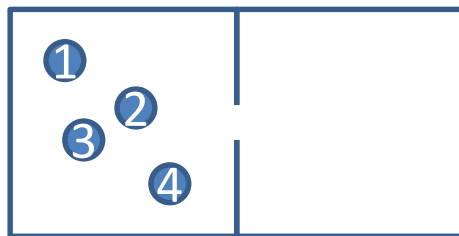
$$S = k_B \ln \Omega$$

Where k_B is the Boltzmann constant

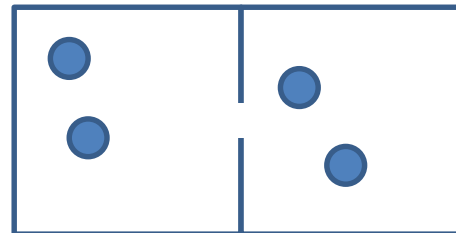
- If you have a system with 4 molecule in a room,

When you observe the system,
the probability you can see
the state = $1/16 = 6.25\%$

The number of possible configurations



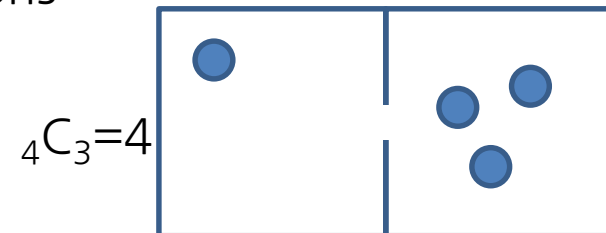
$${}^4C_0 = 1$$



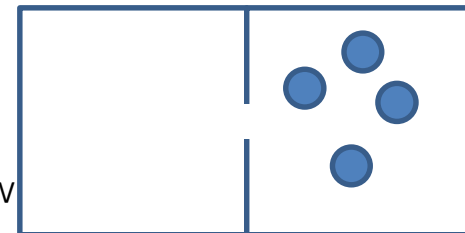
$${}^4C_2 = 6$$

Entropy is high

the probability you can see
this state = $6/16 = 37.5\%$



$${}^4C_3 = 4$$



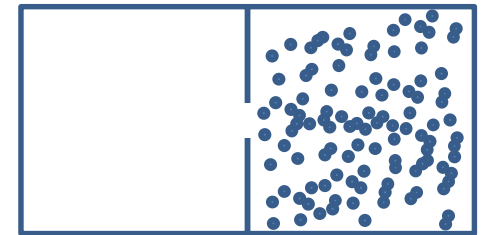
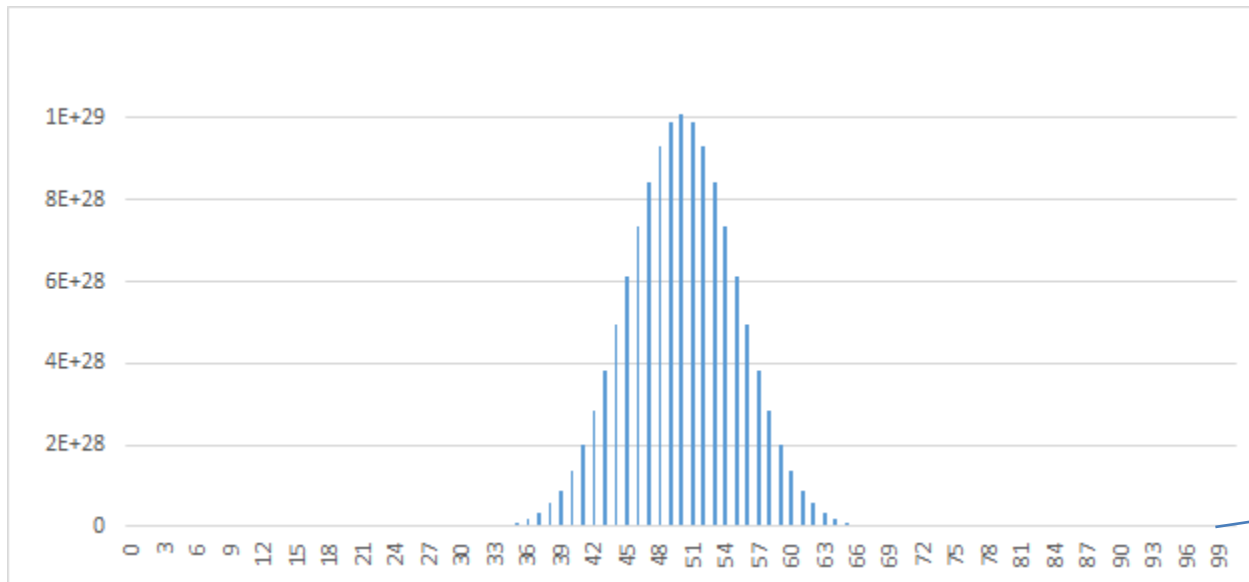
$${}^4C_4 = 1$$

Entropy is low

$${}^4C_1 = 4$$

Statistical understanding of S

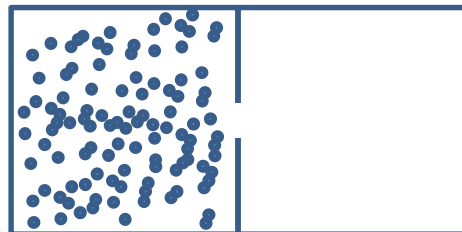
- When there are 100 molecules,



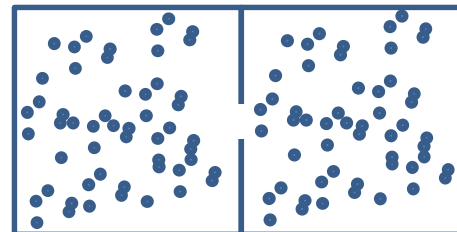
The probability you can observe this state: $7.9 \times 10^{-29}\%$

Actually there are 6.022×10^{23} gas molecules in 0.224m^3

All the system moves to maximize its entropy



$\Delta S > 0$



Low entropy
(Possible but very rare)

High entropy

Second Law

- Entropy can be defined by two different points of view, but it is proved as same.

$$- dS = \frac{dQ_{rev}}{T}$$

$$- S = k_B \ln \Omega$$

If you want to know how it can be same, you need read more references:

Textbook (Chapter 3.3, 3.11) and



Arieh Ben-Naim, A Farewell to Entropy : Statistical Thermodynamics Based on Information, Chapter 5, World Scientific Publishing Company, 2008.

(you can find an e-book from SNU library)

- **2nd law says:**

$$- ds \equiv \frac{\delta q_{rev}}{T} \rightarrow \Delta s \equiv \int \frac{\delta q_{rev}}{T} = \frac{q_{rev}}{T} = \text{constant}$$

- $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \geq 0$

- For a reversible process, $\Delta S_{univ} = 0$

- For an irreversible process, $\Delta S_{univ} > 0$

Why entropy is important?

- Actually, all the real processes are irreversible, but we cannot know the exact path of the real process.
- We can “assume” an ideal reversible ($dS=0$) process for each equipment and this is the best case for the equipment.
- Then we can compare the real result with the ideal best case, then can say its “efficiency”

Entropy for a reversible process

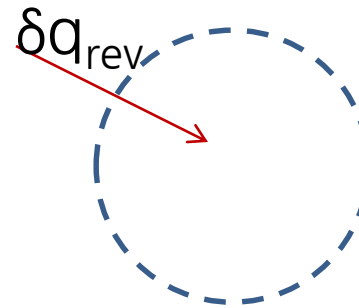
- Reversible, isothermal

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

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

- $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$

- $\Delta S_{sys} \neq 0, \Delta S_{surr} \neq 0$



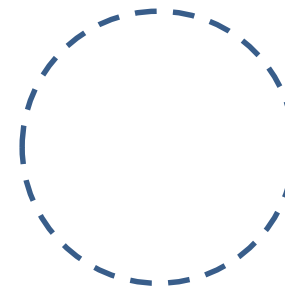
- Reversible and Adiabatic = **Isentropic**

- $\Delta S_{sys} = \frac{q_{rev}}{T} = 0$

- $\Delta S_{surr} = -\frac{q_{rev}}{T} = 0$

- $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$

- $\Delta S_{sys} = 0, \Delta S_{surr} = 0$

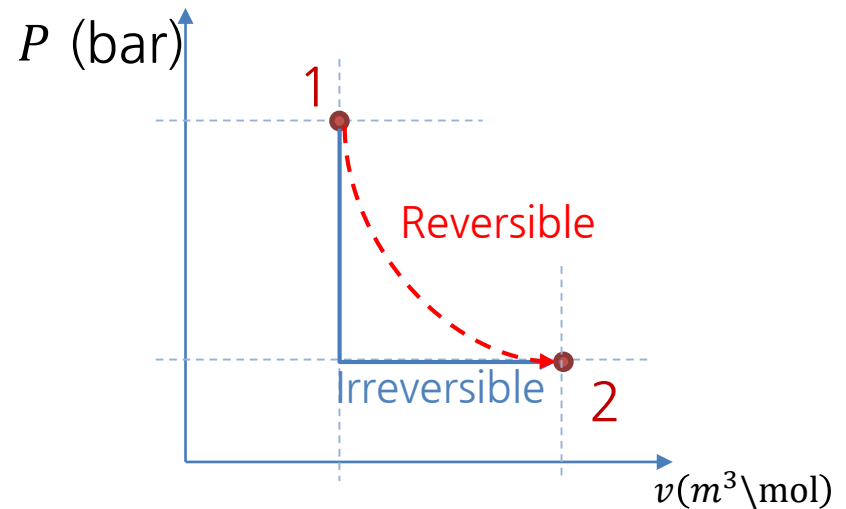


➡ **Isentropic**

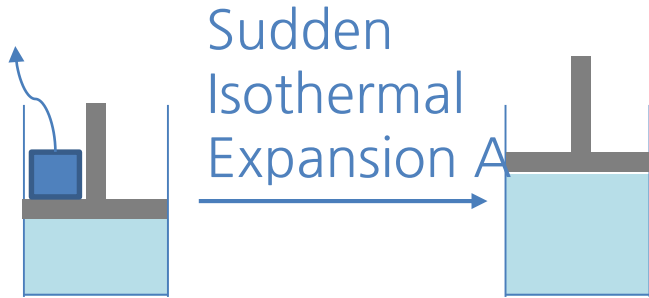
How to get Δs from T, P, v without q_{rev} ?

- Entropy is a state function
- For a real(irreversible) process from state 1 to 2, we can construct a hypothetical reversible process from 1 to 2 to get Δs

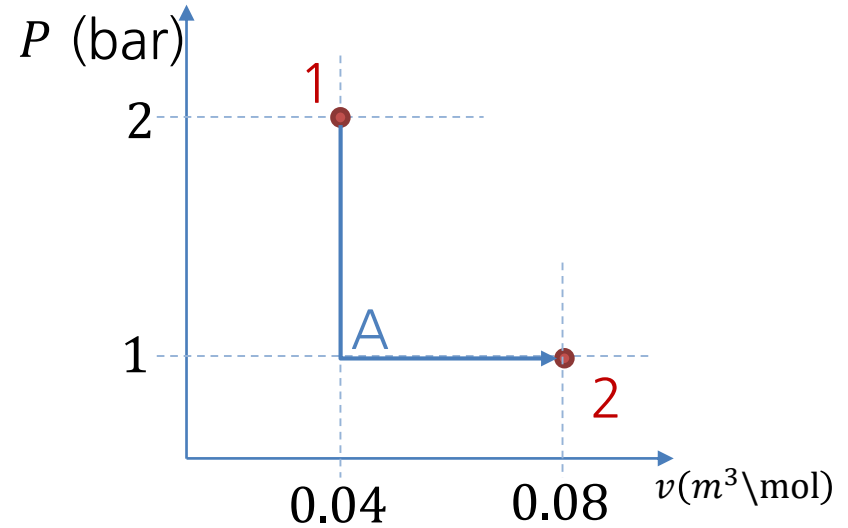
$$\begin{aligned}\Delta S_{real(blue)} &= S_2 - S_1 \\ &= \Delta S_{rev(red)}\end{aligned}$$



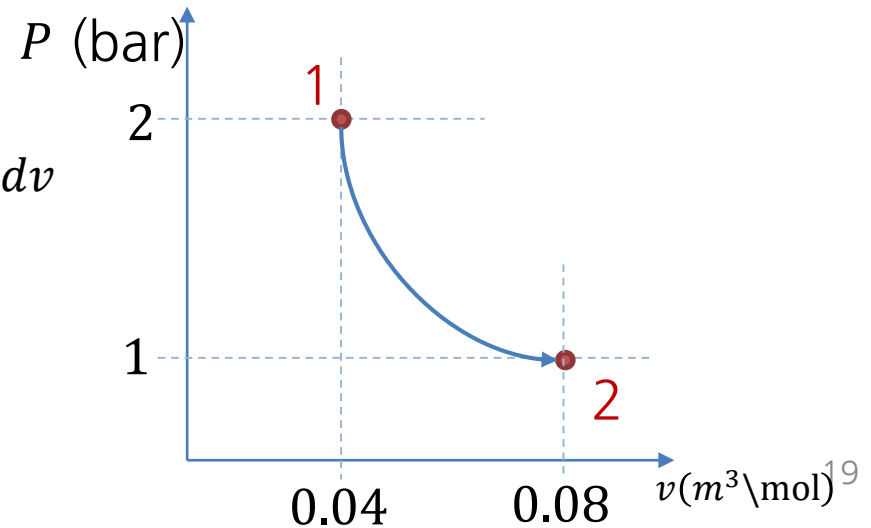
Entropy of irreversible Process



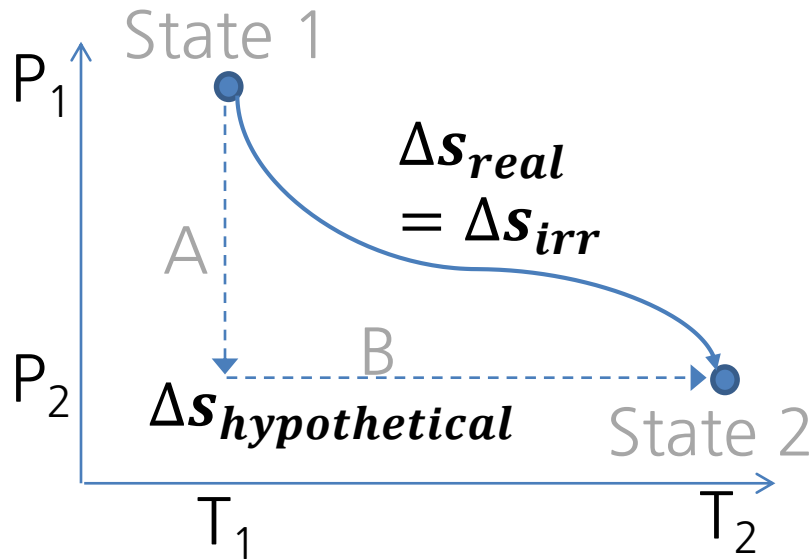
$$\begin{aligned}
 q_{A,actual} &= -w_{A,actual} \\
 &= 1(\text{bar}) \cdot (0.08 - 0.04)(\text{m}^3/\text{mol}) \\
 &= 4000 (\text{J}/\text{mol}) \neq q_{rev}
 \end{aligned}$$



$$\begin{aligned}
 q_{A,rev} &= -w_{rev} = + \int_{v_1}^{v_2} P dv = \int_{v_1}^{v_2} \frac{P_1 v_1}{v} dv \\
 &= P_1 v_1 \ln \left(\frac{v_2}{v_1} \right) = 5545 (\text{J}/\text{mol})
 \end{aligned}$$



How to get Δs for an irreversible process?



Step A: reversible isothermal expansion

$$du = 0 = \delta q_{rev} + \delta w_{rev}$$

$$\delta q_{rev} = -\delta w_{rev} = P dv$$

$$\Delta s_A = \int \frac{\delta q_{rev}}{T} = \int \frac{P dv}{T}$$

For Ideal gas, $Pv=RT$

$$\Delta s_A = \int_{v_1}^{v_2} \frac{R}{v} dv = R \ln \frac{v_2}{v_1} = -R \ln \frac{P_2}{P_1}$$

Step B: reversible isobaric expansion

$$du = \delta q_{rev} + \delta w_{rev} = \delta q_{rev} - P dv$$

$$dh = d(u + Pv) = du + P dv + V dp$$

$$\delta q_{rev} = dh = c_p dT$$

$$\Delta s_B = \int \frac{\delta q_{rev}}{T} = \int_{T_1}^{T_2} \frac{c_p}{T} dT$$

$$\Delta s = \Delta s_A + \Delta s_B = \int_{T_1}^{T_2} \frac{c_p}{T} dT - R \ln \frac{P_2}{P_1}$$

If c_p is constant,

$$\Delta s = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$