

**강의 note 2006**

# **화공 열역학 1**



**한경대학교 화학공학과**

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# 화공열역학 (야간)

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  - 출석(8), 과제(12), 발표(0), 중간(40), 기말(40)

# 강의방법

- 교재중심적 (1장-2장)
- 과제/발표를 통한 충분한 예제풀이 (각 장 연습문제 지정된 문제만 과제로 제출 및 발표)
- 교재: matlab 을 이용한 화학공학 열역학, 김현외 4인 공정, 아진

# 열역학의 응용 목적

- 화학/생물 분자에 관한 기본 물성치에 관한 정보구축 (database: KDB, NIST, DIPPR)
- 물성치 예측모델 개발
- 물성치 예측
  - NIST: <http://webbook.nist.gov/chemistry/>,
  - 한국화학공학정보센터: <http://www.cheric.org>
- 상평형의 이론적 접근
- 활동도 (액상내 실질 농도) 예측
- 공정개발이나 합성에 응용

# 열역학 서론 목차

*What we are to Learn*

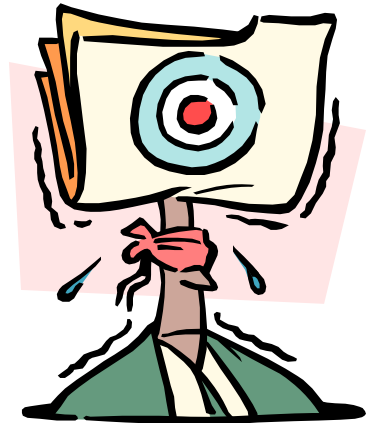
☺ 열역학 어떻게 할 것인가(개략적 논의)

1. 물질 및 에너지 보존
2. 진화법칙과 엔트로피 개념
3. 순수한 유체의 부피 성질
4. 순수한 유체의 열적 성질
5. 유체의 열역학적 성질



# 개략적 논의

열역학 어떻게 할 것인가 ?



# 무엇을 이야기할 것인가 ?

*What we are to Learn*

1. 거시적인 계의 해석
2. **Energy** and the 1<sup>st</sup> Law of Thermodynamics
3. **Entropy** and the 2<sup>nd</sup> Law of Thermodynamics
4. **Free Energy** and **Equilibrium**
5. **Applications** of Thermodynamics to  
Chemical Engineering Problems  
**Discussions**  
**Problems**

# 백과 사전적 의미: 열역학

## *Encyclopedia Description of Thermodynamics*

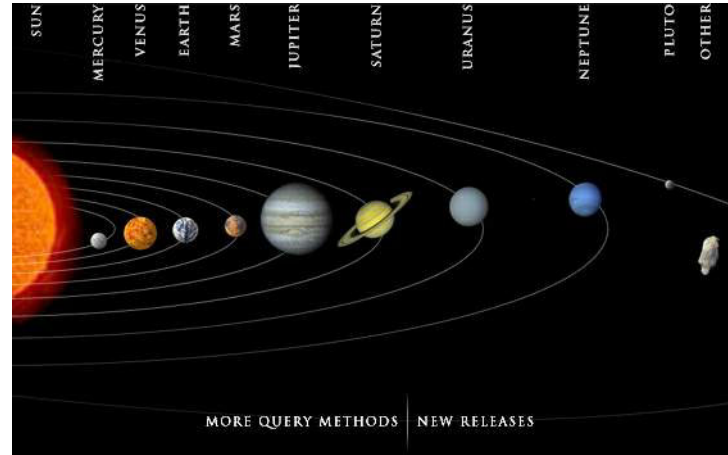
Study of the relationships among heat, work, temperature, and energy. Any physical system will spontaneously approach an equilibrium that can be described by specifying its properties, such as pressure, temperature, or chemical composition. If external constraints are allowed to change, these properties generally change.

The three laws of thermodynamics describe these changes and predict the equilibrium state of the system. The first law states that whenever energy is converted from one form to another, the total quantity of energy remains the same.

The second law states that, in a closed system, the entropy of the system does not decrease. The third law states that, as a system approaches absolute zero, further extraction of energy becomes more and more difficult, eventually becoming theoretically impossible



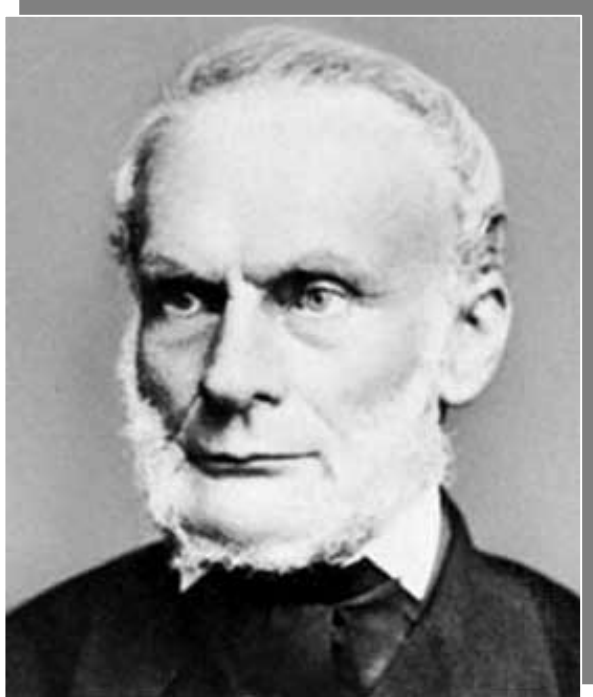
- 에너지 보존법칙: 지구와 태양계의 에너지 보존 (달한계와 열린계)



- 엔트로피 증가 법칙: 우주의 기원과 팽창

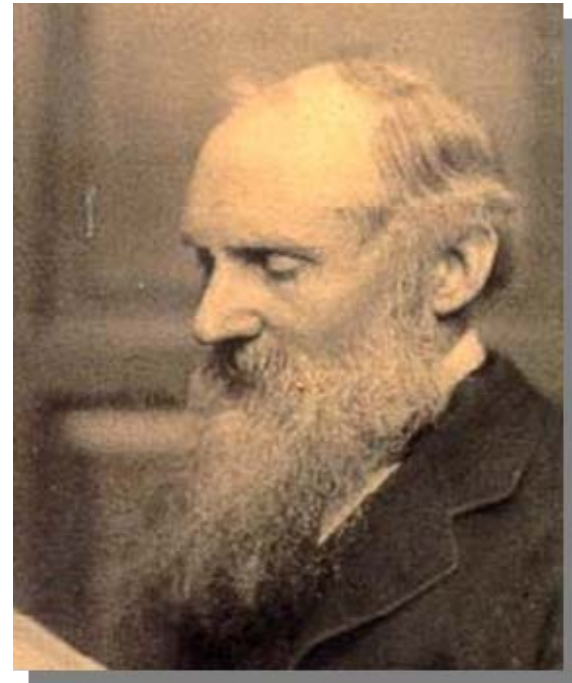


# Pioneers on Classical Thermodynamics



*Rudolf Clausius*  
(1822-1888)

*“Die Energie im Welt ist Konstant”*  
*“Die Entropie im Welt Strebt Maximum Zu”*



*Thomson, Sir William*  
(*Baron Kelvin, 1824-1907*)

*“Absolute Temperature”*  
*“Heat, Work Equivalency”*

# 열역학의 역사적 측면



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*James Prescott Joule*  
*(1818-1889)*

*Joule's Law :*

*“Energy used up in one  
form reappears in another  
and is never lost”*

# 보편적 에너지 보존법칙(열역학 제1법칙)

“Die Energie im Welt Ist Konstant”

“Internal changes =  $\sum$  Interactions occurring at boundaries”

$$“\Delta U = Q - W”$$

## 1. Consequences

- **Internal energy:** All forms of **energy possesses by matter** as a consequence of random molecular motion or intermolecular forces; it is defined as the **state function**
- **Energy in transit :** Heat(**Q**) is the flow of thermal energy by virtue of **T-difference**; **work** is the flow of mechanical energy due to **driving force** other than temperature, these are defined as the **path functions**
- **Conversion:** Energy could change its form, but the total amount is always remained fixed.
- **Degradable Nature:**  $\text{Energy} = \text{Exergy} + \text{Anergy}$

## 2. Energy Balance

**Rate of internal energy changes |<sub>System</sub> =  
Σ Interactions of path-dependent energies  
occurring at boundaries”**

$$\frac{d}{dt} [u + m(e_K + e_P)]_{System} = \sum_l^L n_l (h + e_K + e_P)_l - \sum_e^E n_e (h + e_K + e_P)_e + \dot{Q} + \dot{W}$$

$$du = \delta \dot{q} - \delta \dot{w}$$

- **differential (d) ≈ infinitesimal(δ)**
- **First law is universal** only when a change occurs between two end equilibrium states (reversible)  
= **Maximum or Minimum work requirement**

# 진화법칙 (열역학 2법칙, 경계조건에 지배)

## 1. 고립된 세상의 진화방향 (isolated enclosure)

“Die Entropie im Welt Strebt Maximum zu”

$$dS(U, V, N) \geq 0$$

“What will be the **direction of spontaneous change of universe**”

“How one can minimize the useful energy degradation in the time-dependent energy conversion - **Reversible limit**”

## Concept of Equilibrium State - End state of evolution

- it does **not vary** with time
- system is uniform (no internal T, P,  $v$ , or conc. gradients)
- all flows of heat, mass or work between **sys. & surr.** is zero
- net rate of all chemical reactions is zero

# Free Energy and Evolution to Equilibrium State

*Less rigid than Entropy Function*

## 1. Combined Statement of 1<sup>st</sup> and 2<sup>nd</sup> Laws

### (1) Free Energy - Alternative S

- Evolution in an isolated System  
(Entropy currency)
- What will be a criterion of evolution in a closed system  
(Can open to energy flux)

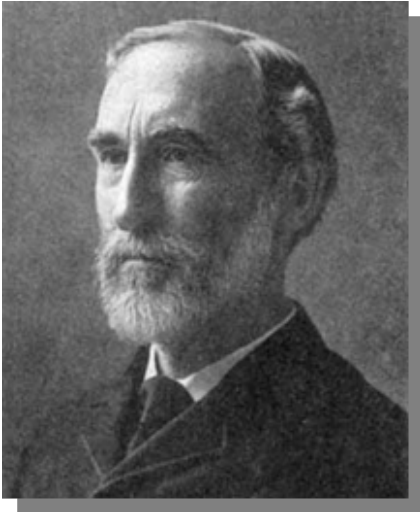
→ Free energy currency



*Hermann Von Helmholtz*  
(1821-1894)



## 2. Gibbs Free Energy, G



*J. Willard Gibbs  
(1838-1903)*

*A closed, isothermal, constant-pressure system*

$$\frac{dU}{dt} \equiv \dot{Q} - P \frac{dV}{dt} \equiv \dot{Q} - \frac{d}{dt}(PV)$$

$$\frac{dS}{dt} \equiv \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

$$\frac{dU}{dt} + \frac{d}{dt}(PV) - \frac{d}{dt}(TS) \equiv \frac{d(U + PV - TS)}{dt} \equiv \frac{d(H - TS)}{dt} \equiv \frac{dG}{dt} \equiv -T \dot{S}_{gen} \leq 0$$

• **Gibbs Free Energy**

$$G \equiv U + PV - TS \equiv H - TS$$

• **G-Minimum Principle**

$$T \geq 0, \quad \dot{S} \geq 0 \quad \rightarrow \quad -T \dot{S}_{gen} \leq 0$$

• **Dissipation Function**

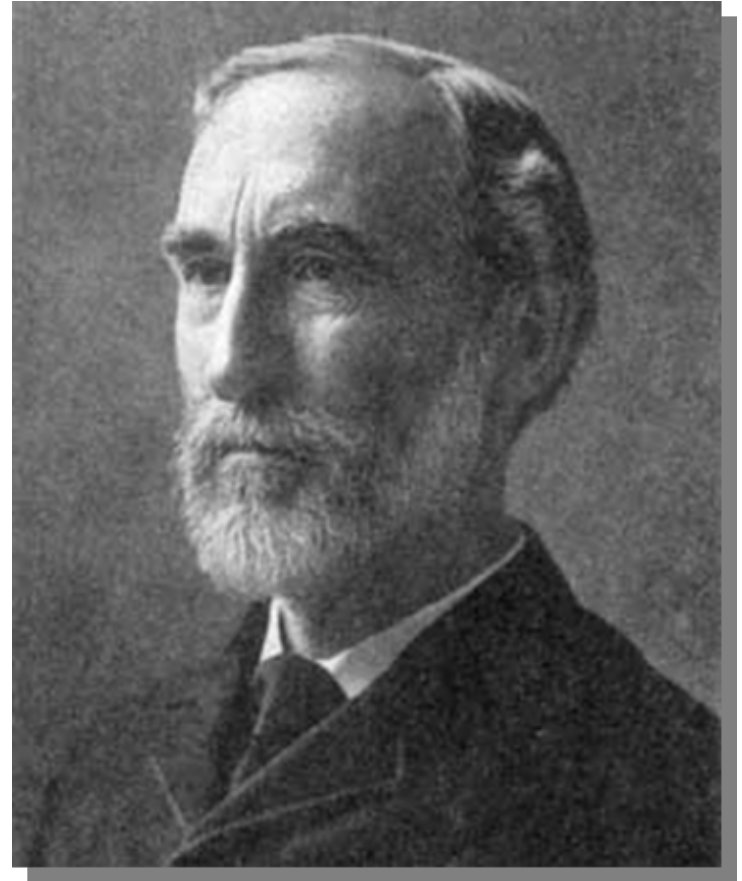
$$\Phi \equiv T \dot{S}_{gen} \geq 0$$

• **New Equilibrium Criterion**

$$\Delta G_{T,P,N} \leq 0$$



평형물성은  
다양한  
공정과  
제품 설계의  
핵심 정보



*J. Willard Gibbs  
(1839-1903)*

**“Mathematics is a language”**

**Gibbsian Thermodynamics**

**J - Joule**

**$T_0$  - Standard State of T**

**H - Enthalpy**

**P - Pressure**

**R - Gas constant**

**U - Internal energy**

**S - Entropy**

**n - Moles**

**T – Temperature**

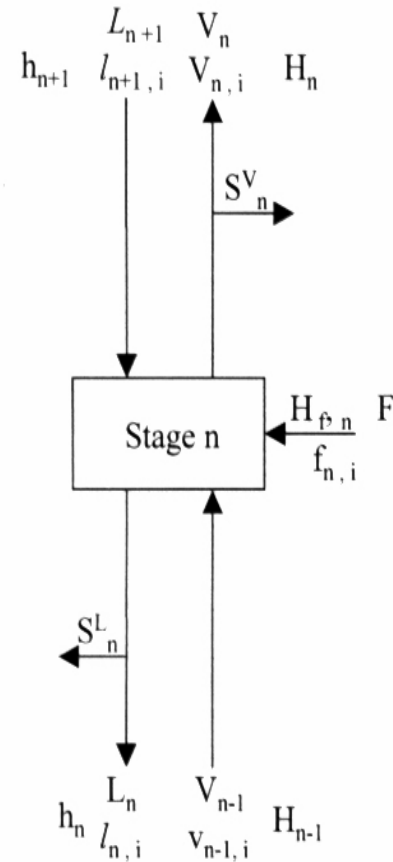
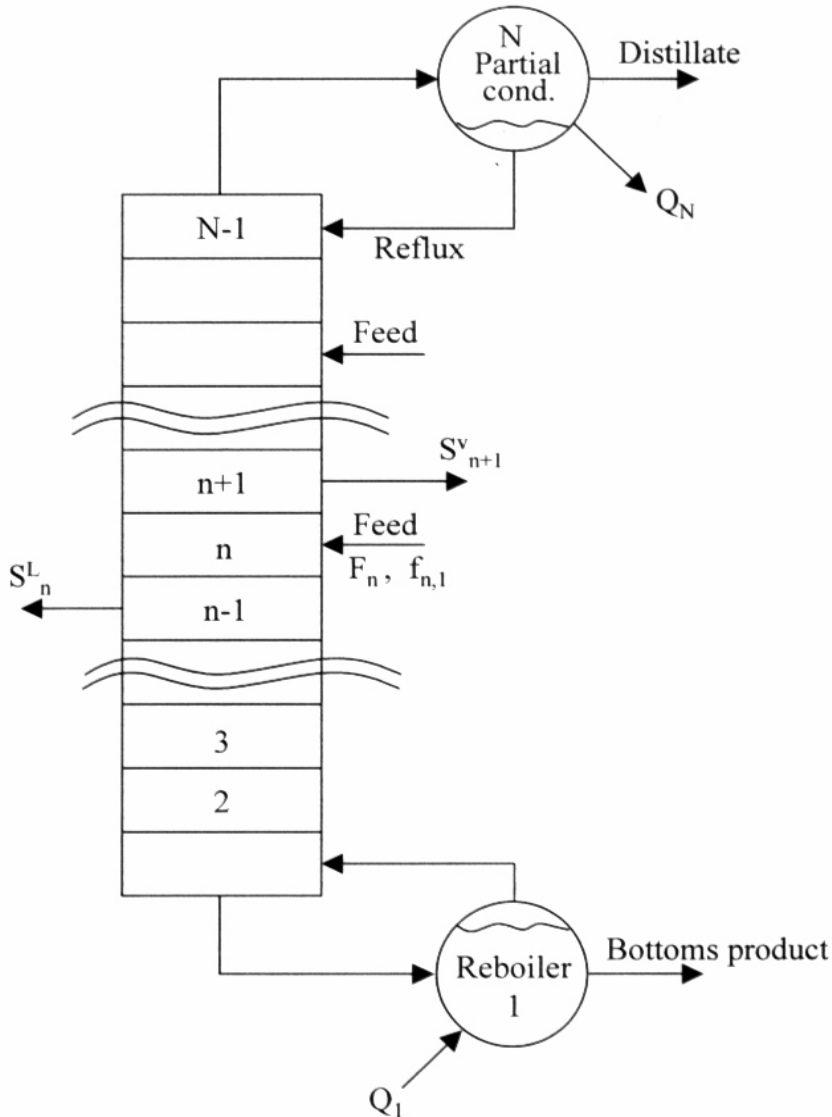
**z - Compressibility factor**



*John M. Prausnitz*

*“Founder of Practical Molecular Thermodynamics”*

# 분리공정 기본설계 : 다성분 다단 증류탑



Subscript  $n$  : flow from stage  $n$ ,  
 $n=1, 2, \dots, N$

Subscript  $i$  : component  $i$ ,  $i=1, 2, \dots, M$

$H$  = vapor phase enthalpy

$h$  = liquid phase enthalpy

$H_f$  = feed enthalpy

$V$  = total vapor flow

$v$  = component vapor flow

$L$  = total liquid flow

$l$  = component liquid flow

$F$  = total feed

$S^L$  = liquid side stream

$S^V$  = vapor side stream

다단 증류탑과  $n$  단 상세도

# Property Databank Websites



- 1. KDB (Korean Thermophysical Properties Databank)**
- 2. DDB (Dortmund Databank)**
- 3. DIPPR (AIChE Design Institute Databank)**

# Remarks

1. 고전 열역학의 핵심 주제인 에너지 보존성질과 변질성 진화와 엔트로피, 평형상태와 상태변수, 자유에너지, 상태변화가 수반되는 계의 물성 변화 등에 대한 이해는
  - 막연한 현상을 공학적으로 접근하고자 할 때,
  - 새로운 분야를 개척하고자 할 때 기본정보 제공
2. 상평형 물성은 다양한 생산공정과 제품의 기본설계 (basic Design) 핵심정보로 생산활동의 경제성 평가에 결정적 영향