



## Chapter 3

The Importance of State Functions:  
Internal Energy and Enthalpy

Physical Chemistry, 3<sup>rd</sup> Edition

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# Objectives

- Express the infinitesimal quantities  $dU$  and  $dH$  as exact differentials.
- Relate the change of  $U$  with  $T$  and  $V$  and the change in  $H$  with  $T$  and  $P$  to experimentally accessible quantities such as the heat capacity and the coefficient of thermal expansion.

$$\Delta U(T,V) \text{ \& } \Delta H(T,P)=f(C, \beta, ..)$$

complemented

# Outline (pp.45-66)

1. The Mathematical Properties of State Functions
2. The Dependence of  $U$  on  $V$  and  $T$
3. Does the Internal Energy Depend More Strongly on  $V$  or  $T$ ?
4. The Variation of Enthalpy with Temperature at Constant Pressure
5. How are  $C_p$  and  $C_v$  Related?
6. The Variation of Enthalpy with Pressure at Constant Temperature
7. The Joule-Thompson Experiment
8. Liquefying Gases Using an Isenthalpic Expansion

## 3.1 The Mathematical Properties of State Functions

- In this chapter  $\Delta U$  and  $\Delta H$  will be calculated as functions of  $P$ ,  $V$ , and  $T$  for real gases, liquids, and solids. First, the math. props. need to be outlined.
- Consider 1 *mol* of an ideal gas for which

$$P = f(V, T) = \frac{RT}{V} \quad (3.1)$$

- The change in  $P$  as a function of  $V$  or  $T$  is expressed by the following **partial derivatives**:  
(편도함수)

$$\begin{aligned} \left( \frac{\partial P}{\partial V} \right)_T &= \lim_{\Delta V \rightarrow 0} \frac{P(V + \Delta V, T) - P(V, T)}{\Delta V} = -\frac{RT}{V^2} \\ \left( \frac{\partial P}{\partial T} \right)_V &= \lim_{\Delta T \rightarrow 0} \frac{P(V, T + \Delta T) - P(V, T)}{\Delta T} = \frac{R}{V} \end{aligned} \quad (3.2)$$



# 3.1 The Mathematical Properties of State Functions

- $P$  changes to  $P+dP$  as  $T$  &  $V$  change.

$$dP = \left( \frac{\partial P}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial V} \right)_T dV \quad (3.3)$$

(3.3) is total differential (전미분) of  $P$ .

- In differential calculus, if a function satisfies **Euler Condition**(3.5), we say it has an exact differential (완전미분).

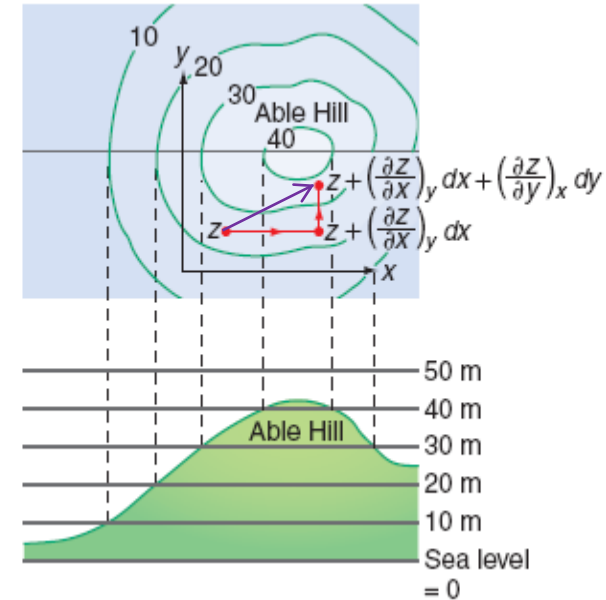


Fig.3.1 Altitude :  $Z(EW \pm x, NS \pm y)$ .

- All the state functions have exact differentials since they are indep of the path: indep of the order of differentiation.

$$\left( \frac{\partial}{\partial T} \left( \frac{\partial P(V, T)}{\partial V} \right)_T \right)_V = \left( \frac{\partial}{\partial V} \left( \frac{\partial P(V, T)}{\partial T} \right)_V \right)_T = -\frac{R}{V^2} \quad \sim \text{Euler Condition} \quad (3.5)$$

~ mixed (or cross) partial derivatives (혼합 또는 교차편도함수)

# Example Problem 3.1

a. Calculate

$$\left(\frac{\partial f}{\partial x}\right)_y, \left(\frac{\partial f}{\partial y}\right)_x, \left(\frac{\partial^2 f}{\partial x^2}\right)_y, \left(\frac{\partial^2 f}{\partial y^2}\right)_x, \frac{\partial^2 f}{\partial y \partial x} = \left(\frac{\partial \left(\frac{\partial f}{\partial x}\right)_y}{\partial y}\right)_x, \text{ and } \frac{\partial^2 f}{\partial x \partial y} = \left(\frac{\partial \left(\frac{\partial f}{\partial y}\right)_x}{\partial x}\right)_y$$

~1<sup>st</sup> derivatives
~2<sup>nd</sup> derivatives

for the function  $f(x, y) = ye^x + xy + x \ln y$ .

b. Determine if  $f(x, y)$  is a state function of the variables  $x$  and  $y$ .

c. If  $f(x, y)$  is a state function of the variables  $x$  and  $y$ , what is the total differential  $df$ ?

# Solution

a.

$$\left(\frac{\partial f}{\partial x}\right)_x = ye^x + y + \ln y, \quad \left(\frac{\partial f}{\partial y}\right)_x = e^x + x + \frac{x}{y}$$

$$\left(\frac{\partial^2 f}{\partial x^2}\right)_y = ye^x, \quad \left(\frac{\partial^2 f}{\partial y^2}\right)_x = -\frac{x}{y^2}$$

$$\left(\frac{\partial\left(\frac{\partial f}{\partial x}\right)_y}{\partial y}\right)_x = e^x + 1 + \frac{1}{y}, \quad \left(\frac{\partial\left(\frac{\partial f}{\partial y}\right)_x}{\partial x}\right)_y = e^x + 1 + \frac{1}{y}$$

# Solution

b. Because we have shown that

$$\left( \frac{\partial \left( \frac{\partial f}{\partial x} \right)_y}{\partial y} \right)_x = \left( \frac{\partial \left( \frac{\partial f}{\partial y} \right)_x}{\partial x} \right)_y$$

$f(x,y)$  is a state function of the variables  $x$  and  $y$ . Note that any well-behaved function that can be expressed in analytical form is a state function.

c. The total differential is given by

$$\begin{aligned} df &= \left( \frac{\partial f}{\partial x} \right)_y dx + \left( \frac{\partial f}{\partial y} \right)_x dy \\ &= \left( ye^x + y + \ln y \right) dx + \left( e^x + x + \frac{x}{y} \right) dy \end{aligned}$$



# 3.1 The Mathematical Properties of State Functions

- Two other differentiation results will be used frequently:

a) For a function of  $z=f(x, y)$ ,

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \quad (3.6)$$

b) The **cyclic rule** (순환규칙)

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \quad (\gamma)$$

if we assume  $z=\text{const}$ ,  $dz=0$  then from  $(\gamma)$

$$\begin{aligned} 0 &= \left(\frac{\partial z}{\partial x}\right)_y (\partial x)_z + \left(\frac{\partial z}{\partial y}\right)_x (\partial y)_z : \div (\partial y)_z \text{ 하면} \rightarrow 0 = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x \\ &\times \left(\frac{\partial y}{\partial z}\right)_x \text{ 하면} \rightarrow 0 = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + 1 \end{aligned}$$

# 3.1 The Mathematical Properties of State Functions

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \quad (3.7)$$

- If we apply cyclic rule to (3.3), then we have

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV \quad (3.3)$$

- From the cyclic rule of  $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$

$$\left(\frac{\partial P}{\partial T}\right)_V = - \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = - \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\beta}{\kappa} \quad (\alpha)$$

$$\left(\frac{\partial P}{\partial V}\right)_T = - \frac{1}{\kappa V} \quad (3.8)$$

# 3.1 The Mathematical Properties of State Functions

- The  $\beta$  and  $\kappa$  are readily measurable properties:

$$\beta \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \text{and} \quad \kappa \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad (3.9)$$

$\beta$  = isobaric thermal expansion coefficient (열팽창계수), Table 3.1

$\kappa$  = isothermal compressibility (압축계수, 압축률), Table 3.2

- If we substitute (3.8) and ( $\alpha$ ) into (3.3), we have

$$dP = \frac{\beta}{\kappa} dT - \frac{1}{\kappa V} dV \quad \sim f(\text{readily measurable qnties}) \quad (3.10)$$

- It can be integrated to give

$$\Delta P = \int_{T_i}^{T_f} \frac{\beta}{\kappa} dT - \int_{V_i}^{V_f} \frac{1}{\kappa V} dV \approx \frac{\beta}{\kappa} (T_f - T_i) - \frac{1}{\kappa} \ln \frac{V_f}{V_i} \quad (3.11)$$

## 3.1 The Mathematical Properties of State Functions

- For a small change in T and P, (3.9) can be written in more compact form:

$$V(T_2) = V(T_1)(1 + \beta[T_2 - T_1]) \text{ and } V(P_2) = V(P_1)(1 - \kappa[P_2 - P_1])$$

Derivation:

$$\beta = \frac{1}{V} \left( \frac{dV}{dT} \right) \rightarrow \frac{dV}{V} = \beta dT \quad \kappa = -\frac{1}{V} \left( \frac{dV}{dP} \right) \rightarrow \frac{dV}{V} = -\kappa dP$$

$$\ln \left( \frac{V}{V_0} \right) = \beta(T - T_0) \rightarrow V = V_0 e^{\beta(T - T_0)}$$

$$V \approx V_0 [1 + \beta(T - T_0)] \text{ if } \beta(T - T_0) \ll 1 \quad (\beta)$$

$$\text{Since } e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \dots; e^x \approx 1 + x \text{ for } x \ll 1$$

- For constant P, let  $T_0$  (or  $T_1$ ) = 273.15 K then ( $\beta$ ) becomes

$$V = V_0(1 + \beta t), \text{ where } V = \text{volume at } t^\circ\text{C}; V_0 = \text{volume at } 0^\circ\text{C}$$

# Table 3.1 Isobaric Volumetric Thermal Expansion Coefficient at 298 K, $\beta$

**TABLE 3.1** ISOBARIC VOLUMETRIC THERMAL EXPANSION COEFFICIENT FOR SOLIDS AND LIQUIDS AT 298 K

Element	$10^6 \beta \text{ (K}^{-1}\text{)}$	Element or Compound	$10^4 \beta \text{ (K}^{-1}\text{)}$
Ag(s)	57.6	Hg(l)	1.81
Al(s)	69.3	CCl <sub>4</sub> (l)	11.4
Au(s)	42.6	CH <sub>3</sub> COCH <sub>3</sub> (l)	14.6
Cu(s)	49.5	CH <sub>3</sub> OH(l)	14.9
Fe(s)	36.9	C <sub>2</sub> H <sub>5</sub> OH(l)	11.2
Mg(s)	78.3	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> (l)	10.5
Si(s)	7.5	C <sub>6</sub> H <sub>6</sub> (l)	11.4
W(s)	13.8	H <sub>2</sub> O(l)	2.04
Zn(s)	90.6	H <sub>2</sub> O(s)	1.66

$O(10^{-4})$

$O(10^{-3})$

Sources: Benenson, W., Harris, J. W., Stocker, H., and Lutz, H., *Handbook of Physics*, Springer, New York, 2002; Lide, D. R., Ed., *Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002; Blachnik, R., Ed., *D'Ans Lax Taschenbuch für Chemiker und Physiker*, 4th ed., Springer, Berlin, 1998.



# Table 3.2 Isothermal compressibility at 298 K, $\kappa$

**TABLE 3.2 ISOTHERMAL COMPRESSIBILITY AT 298 K**

Substance	$10^6 \kappa/\text{bar}^{-1}$	Substance	$10^6 \kappa/\text{bar}^{-1}$
Al(s)	1.33	Br <sub>2</sub> (l)	64
SiO <sub>2</sub> (s)	2.57	C <sub>2</sub> H <sub>5</sub> OH(l)	110
Ni(s)	0.513	C <sub>6</sub> H <sub>5</sub> OH(l)	61
TiO <sub>2</sub> (s)	0.56	C <sub>6</sub> H <sub>6</sub> (l)	94
Na(s)	13.4	CCl <sub>4</sub> (l)	103
Cu(s) $O(10^{-6})$	0.702	CH <sub>3</sub> COCH <sub>3</sub> (l) $O(10^{-4})$	125
C(graphite)	0.156	CH <sub>3</sub> OH(l)	120
Mn(s)	0.716	CS <sub>2</sub> (l)	92.7
Co(s)	0.525	H <sub>2</sub> O(l)	45.9
Au(s)	0.563	Hg(l)	3.91
Pb(s)	2.37	SiCl <sub>4</sub> (l)	165
Fe(s)	0.56	TiCl <sub>4</sub> (l)	89
Ge(s)	1.38		

Sources: Benenson, W., Harris, J. W., Stocker, H., and Lutz, H., *Handbook of Physics*, Springer, New York, 2002; Lide, D. R., Ed., *Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002; Blachnik, R., Ed., *D'Ans Lax Taschenbuch für Chemiker und Physiker*, 4th ed., Springer, Berlin, 1998.

## Example Problem 3.2

You have accidentally arrived at the end of the range of an ethanol in glass thermometer so that the entire volume of the glass capillary is filled. By how much will the pressure in the capillary increase if the temperature is increased by another  $10.0^{\circ}\text{C}$ ?

$$\beta_{\text{glass}} = 2.00 \times 10^{-5} (\text{^{\circ}C})^{-1}, \quad \beta_{\text{ethanol}} = 11.2 \times 10^{-4} (\text{^{\circ}C})^{-1}, \text{ and}$$

$$\kappa_{\text{ethanol}} = 11.00 \times 10^{-5} (\text{bar})^{-1}.$$

Do you think that the thermometer will survive your experiment?

# Solution

From (3.11),

$$\begin{aligned}
 \Delta P &= \int \frac{\beta_{ethanol}}{\kappa} dT - \int \frac{1}{\kappa V} dV \approx \frac{\beta_{ethanol}}{\kappa} \Delta T - \frac{1}{\kappa} \ln \frac{V_f}{V_i} \\
 &= \frac{\beta_{ethanol}}{\kappa} \Delta T - \frac{1}{\kappa} \ln \frac{V_i (1 + \beta_{glass} \Delta T)}{V_i} \approx \frac{\beta_{ethanol}}{\kappa} \Delta T - \frac{\beta_{glass} \Delta T}{\kappa} \quad \text{red arrow} \\
 &= \frac{(\beta_{ethanol} - \beta_{glass})}{\kappa} \Delta T = \frac{(11.2 - 0.2) \times 10^{-4} \text{ } ^\circ\text{C}^{-1}}{11.0 \times 10^{-5} \text{ bar}^{-1}} \times 10.0^\circ\text{C} = 65.5 \text{ bar}
 \end{aligned}$$

In this calculation, we have used the relations:

$$V(T_2) = V(T_1)(1 + \beta[T_2 - T_1]) ; \ln(1 + x) \approx x \text{ if } x \ll 1 \quad (\beta)$$

The glass is unlikely to withstand such a large increase in pressure.

우측 1항은 승온에 따른 알코올 부피 증가에 의한 승압  
 우측 2항은 유리관 부피 증가에 따른 모세관 내 감압

## 3.2 The Dependence of $U$ on $V$ and $T$ : $U(T,V)$

- As  $U$  is a state function, an infinitesimal change in  $U$  can be written as

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \equiv dU_V + dU_T \quad (3.12)$$

- The differential expression of the 1<sup>st</sup> law can be written as

$$dU = \delta q - P_{ext} dV = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \quad (3.13)$$

- We first consider a constant volume process, then (3.13) becomes

$\Delta U_V$

$$\delta q_V = \left( \frac{\partial U}{\partial T} \right)_V dT = dU_V \quad (cf) \quad \Delta U = \Delta U_V + \Delta U_T \quad (3.14)$$

## 3.2 The Dependence of $U$ on $V$ and $T$ : $U(T,V)$

- $\delta q_v/dT$  corresponds to a constant volume path and is called the **heat capacity at constant volume**,  $C_v$

$$C_v \equiv \frac{\delta q_v}{dT} = \left( \frac{\partial U}{\partial T} \right)_v \quad (3.15)$$

- Atoms with only translational degrees of freedom have low  $C_{V,m}$ , indep of temp. (*He* gas)
- Gases with vibrational degrees of freedom have higher  $C_{V,m}$ . (*CO* & *CO<sub>2</sub>*)

(cf) LN p.2.22

- $C_{V,m}$  always positive.

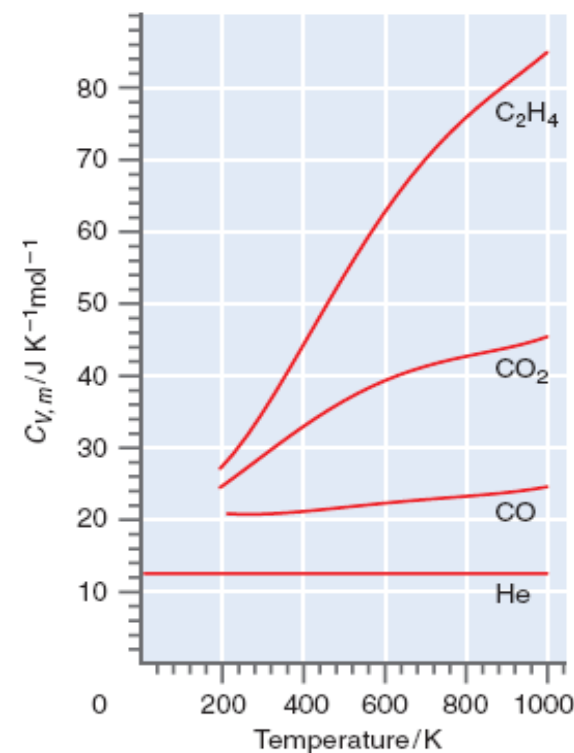


Fig.2.8  $C_{V,m}$  for some gases.



## 3.2 The Dependence of $U$ on $V$ and $T$ : $U(T,V)$

- After  $C_V$  has been determined as a function of  $T$ , the integral is numerically evaluated:

$$\Delta U_V = \int_{T_1}^{T_2} C_V dT = n \int_{T_1}^{T_2} C_{V,m} dT \quad (3.16)$$

- Over a small temperature range,  $C_{V,m}$  can be regarded as a constant and (3.16) is simplified to

$$\Delta U_V = C_V \Delta T = n C_{V,m} \Delta T \quad (3.17)$$

$$q_V = \Delta U \quad \sim \text{bomb calorimeter (Fig.4.3, p.75, Ch.4)} \quad (3.18)$$

- Now let's consider  $(\partial U / \partial V)_T$ , which has a unit of  $\Delta U_T$   $\frac{J}{m^3} = \frac{\text{force}}{\text{area}} = \text{pressure}$ , which is called 'internal pressure'.

~ Will be derived in [5.12]. (cf) (5.61), p.116

## 3.2 The Dependence of $U$ on $V$ and $T$ : $U(V, T)$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad \sim \text{will be derived in [5.12]} \quad (3.19)$$

- The total differential of  $U$  can now be written as

$$dU = dU_V + dU_T = C_V dT + \left[ T\left(\frac{\partial P}{\partial T}\right)_V - P \right] dV \quad (3.20)$$

$$\uparrow (\partial P / \partial T)_V = \beta / \kappa$$

- As  $U$  is a state function, all paths connecting  $(V_i, T_i)$  and  $(V_f, T_f)$  are equally valid in calculating  $\Delta U$ .

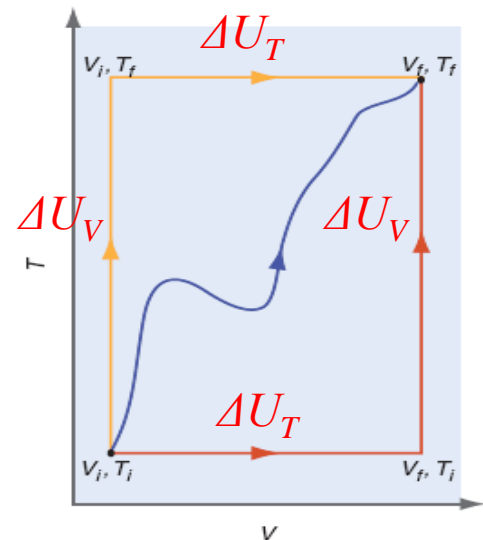


Fig.3.2  $U$  is a state function.

## Example Problem 3.3

Evaluate  $(\partial U / \partial V)_T$  for an ideal gas and modify (3.20) accordingly for the specific case of an ideal gas.

Solution:

$$\text{From (3.20)} \quad dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV = C_V dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV$$

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P = T \left( \frac{\partial [nRT / V]}{\partial T} \right)_V - P = \frac{nRT}{V} - P = 0$$

이상기체는  $imf=0$  이므로 분자간 거리가 바뀌는 데 (즉  $V$ 의 증가나 감소) 에너지가 필요치 않음.

Therefore,  $dU = C_V dT$  shows that  $U$  is a function of  $T$  only for an ideal gas.

### 3.3 Does the Internal Energy Depend More Strongly on $V$ or $T$ ?

- $U$  is a function of  $T$  alone for an ideal gas.
- Not true for real gases, liquids, or solids as the change in  $U$  with  $V$  must be considered.
- Ideal gas molecules do not attract or repel one another, no energy is required to change their average distance of separation (increase or decrease in  $V$ ).

#### 『Joule experiment, 1845』

Target :  $\left(\frac{\partial U}{\partial V}\right)_T$  measurement

system :  $N_2$  gas

Cause of failure :

- large heat capacity of water wrt  $N_2$  gas
- thermometer not accurate enough

👉 Example Problem 3.4

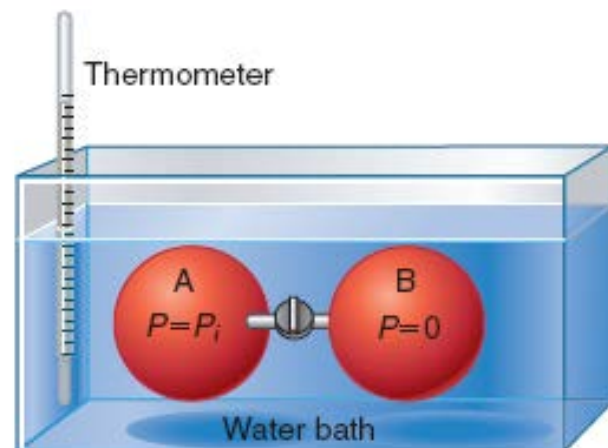


Fig.3.3 Joule experiment.

### 3.3 Does the Internal Energy Depend More Strongly on $V$ or $T$ ?

- From TD 1<sup>st</sup> law,

$$dU = \delta q - P_{ext} dV = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \quad (3.13)$$

- Due to the free expansion,  $P_{ext}=0$  and (3.13) becomes

$$dU = \delta q = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \quad (3.22)$$

- Since Joule found  $\Delta T=0$  in water bath which is in eqm w/ the sys, he concluded

$$\text{Namely } dT_{surr} = dT = 0 \rightarrow \delta q = 0$$

$$\left( \frac{\partial U}{\partial V} \right)_T dV \underset{\uparrow \because dV \neq 0}{=} 0 \rightarrow \left( \frac{\partial U}{\partial V} \right)_T = 0 \sim \text{Joule's law} \quad (3.23)$$



## Example Problem 3.4

In James Joule's experiment to determine  $(\partial U / \partial V)_T$ , the heat capacities of the gas and the water bath surroundings were related by  $C_{\text{surroundings}} / C_{\text{system}} \approx 1000$ .

If the precision with which the temperature of the surroundings could be measured is  $\pm 0.006^\circ\text{C}$ , what is the minimum detectable change in the temperature of the gas?

---

Note that  $C_{\text{surroundings}} = C_{P,\text{surroundings}} \times m_{\text{surroundings}}$  and  $C_{\text{system}} = C_{P,\text{system}} \times m_{\text{system}}$

# Solution

View the experimental apparatus as two interacting systems in a rigid adiabatic enclosure. The first is the volume (gas) within vessels A and B, and the second is the water bath and the vessels. Because the two interacting systems are isolated from the rest of the universe,

$$q = C_{water\ bath} \Delta T_{water\ bath} + C_{gas} \Delta T_{gas} = 0$$

$$\Delta T_{gas} = \frac{C_{water\ bath}}{C_{gas}} \Delta T_{water\ bath} = 1000(\pm 0.006^{\circ}C) = \mp 6^{\circ}C \leftarrow \textit{too large!}$$

'15/03/30

- \* 실험장치를 Fig.2.4, p.22에서와 같이 vessel A와 B 내부의 기체인 system1과 그 나머지로 구성되는 system2의 합성계로 보면 그 합성계는 고립계이므로 외부는 무시할 수 있다. 따라서 고립계 내부의 열흐름만 고려하면 된다.

## Example Problem 3.5: $\Delta U_T$ for real gas

For a real gas described by *vdW* eos (1.12),

$$P = nRT/(V - nb) - an^2/V^2 :$$

- Calculate  $(\partial U / \partial V)_T$  using  $(\partial U / \partial V)_T = T(\partial P / \partial T)_V - P$ .
- Derive an expression for  $\Delta U_T = \int_{V_i}^{V_f} (\partial U / \partial V)_T dV$ .

Solution :

$$\begin{aligned} \text{a.} \quad T \left( \frac{\partial P}{\partial T} \right)_V - P &= T \left( \frac{\partial \left[ \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \right]}{\partial T} \right)_V - P = \frac{nRT}{V - nb} - P \\ &= \frac{nRT}{V - nb} - \frac{nRT}{V - nb} + \frac{n^2 a}{V^2} = \frac{n^2 a}{V^2} \quad \leftarrow \left( \frac{\partial U}{\partial V} \right)_T \end{aligned}$$

## Example Problem 3.5: $\Delta U_T$ for real gas

b.

$$\Delta U_T = \int_{V_i}^{V_f} \left( \frac{\partial U}{\partial V} \right)_T dV = \int_{V_i}^{V_f} \frac{n^2 a}{V^2} dV = n^2 a \left( \frac{1}{V_i} - \frac{1}{V_f} \right)$$

### Analysis

$(\partial U / \partial V)_T = 0$  for an ideal gas from EP3.3, p.52.

But  $(\partial U / \partial V)_T = \frac{n^2 a}{V^2} \neq 0$  for real gases in EP3.5, p.53.

Also, compare  $\Delta U_T$  and  $\Delta U_V$  for real gases in EP3.6!

$$\Delta U_T = n^2 a \left( \frac{1}{V_i} - \frac{1}{V_f} \right); \quad \Delta U_V = \int_{T_1}^{T_2} C_V dT = n \int_{T_1}^{T_2} C_{V,m} dT \quad (3.16)$$

## Example Problem 3.6: $\Delta U_T$ vs. $\Delta U_V$ for real gas

One mol of  $N_2$  gas undergoes a change from (200 K, 5 bar) to (400 K,  $7.88 \times 10^{-4} \text{ m}^3$ ). Treat  $N_2$  as vdW gas w/ the parameters of  $a = 0.017 \text{ Pa m}^6/\text{mol}$  &  $b = 3.87 \times 10^{-5} \text{ m}^3/\text{mol}$ .

a. Calculate  $\Delta U_T = \int_{V_i}^{V_f} \left( \frac{\partial U}{\partial V} \right)_T dV$ . Note that  $V_i = 3.28 \times 10^{-3} \text{ m}^3$  at 200 K as calculated using the vdW eos and consider isothermal compression to  $V_f = 7.88 \times 10^{-4} \text{ m}^3$ .

b. Calculate  $\Delta U_V = n \int_{T_1}^{T_2} C_{V,m} dT$  using the following relationship:

$$C_{V,m} (\text{J} / \text{K} / \text{mol}) = 22.50 - 1.187 \times 10^{-2} T + 2.3968 \times 10^{-5} T^2 \\ + 1.187 \times 10^{-2} T - 1.0176 \times 10^{-8} T^3$$

c. Compare the  $\Delta U_T$  and  $\Delta U_V$ .  LN p.3.31



# Solution

a. Using the result of EP 3.5,

$$\Delta U_T = n^2 a \left( \frac{1}{V_i} - \frac{1}{V_f} \right) = 0.137 \text{ Pa} \cdot \text{m}^6 \times \left( \frac{1}{3.28 \times 10^{-3} \text{ m}^3} - \frac{1}{7.88 \times 10^{-4} \text{ m}^3} \right) \\ = -132 \text{ J}$$

$$\text{b. } \Delta U_V = n \int_{T_i}^{T_f} C_{V,m} dT = \int_{200}^{400} \left( 22.50 - 1.187 \times 10^{-2} T + 2.3968 \times 10^{-5} T^2 \right. \\ \left. + 1.187 \times 10^{-2} T - 1.0176 \times 10^{-8} T^3 \right) dT \\ = (4.50 - 0.712 + 0.447 - 0.0610) \text{ kJ} = 4.17 \text{ kJ}$$

c.  $\Delta U_T$  is 3.2% of  $\Delta U_V$  in this case. For most processes  $\Delta U_T$  can be neglected relative to  $\Delta U_V$  for real gases.

*Q : Which of  $V$  and  $T$  does more strongly affect  $\Delta U$  ?*

### 3.3 Does the Internal Energy Depend More Strongly on $V$ or $T$ ?

- For real gases under most conditions,  $\Delta U_T^{real\ gases} \approx 0$ .
- For processes involving liquids and solids,

$$\Delta U_T^{sol, liq} = \int_{V_1}^{V_2} \left( \frac{\partial U}{\partial V} \right)_T dV \approx \left( \frac{\partial U}{\partial V} \right)_T \Delta V \approx 0 \because \Delta V \approx 0 \quad (3.24)$$

- As a conclusion,  $U$  is almost a function of  $T$  alone for all substances in all phases in case of no chemical rxn nor phase changes.

$$\Delta U \approx \int_{T_i}^{T_f} C_V dT = n \int_{T_i}^{T_f} C_{V,m} dT \quad (3.25)$$

- $\Delta U$  in the cases of chem rxn and/or phase changes will be discussed in Chapters 4 and 6.

$A : T$  does more strongly affect  $\Delta U$ .

### 3.4 The Variation of Enthalpy with Temperature at Constant Pressure, $\Delta H_p$ in $H(T,P)$

- The initial and final states for a process that takes place at constant pressure are shown below.

$$\Delta H_p$$

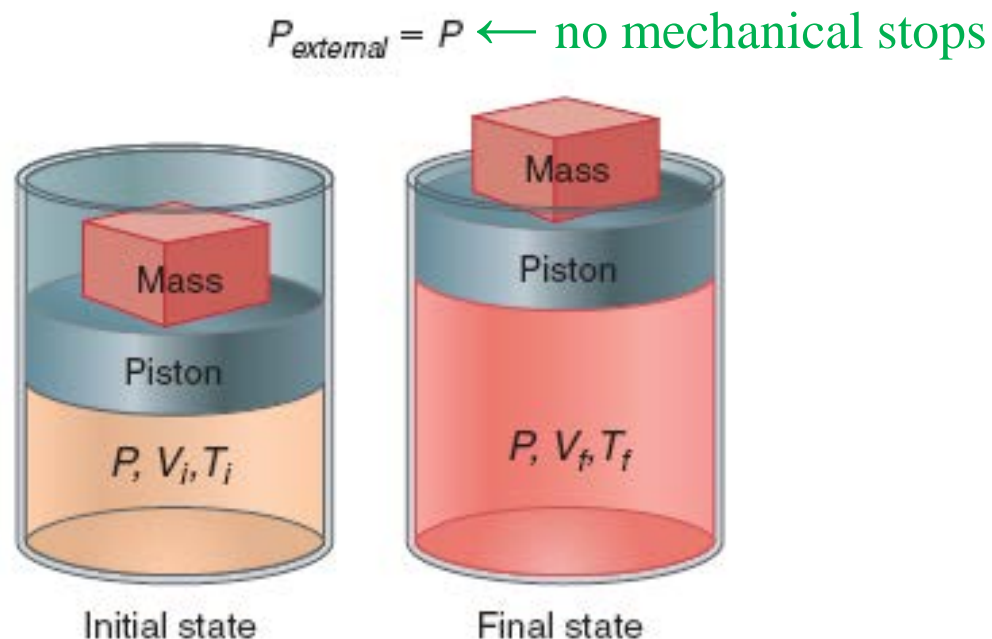
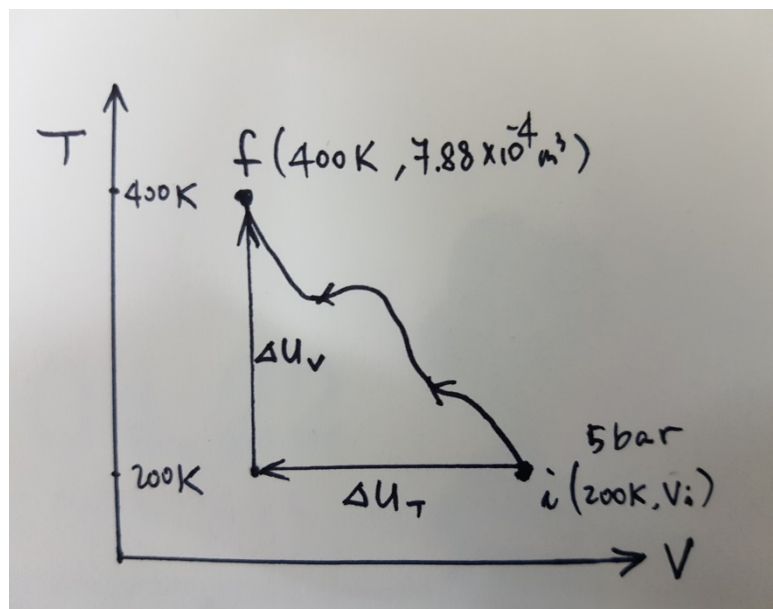


Fig.3.4 Isobaric process.

- The TD 1<sup>st</sup> law becomes :  $dU = \delta q_p - PdV$  (3.26)

### 3.4 The Variation of Enthalpy with Temperature at Constant Pressure, $\Delta H_P$ in $H(T,P)$

$$\int_i^f dU = \int_i^f \delta q_P - \int_i^f P dV \quad \text{or} \quad U_f - U_i = q_P - P(V_f - V_i) \quad (3.27)$$

- As  $P = P_f = P_i$ , we have (cf)  $\Delta U = q_V$  (3.18)

$$(U_f + P_f V_f) - (U_i + P_i V_i) = q_P \quad \text{or} \quad \Delta H = q_P \quad (2.31, 3.28)$$

- Since phase changes such as vaporization & fusion occur at constant T under constant P,  $\Delta H = \Delta U + \Delta(PV)$ .

$$\Delta H_{\text{vap'n}} - \Delta U_{\text{vap'n}} = P \Delta V_{\text{vap'n}} > 0 \because \Delta V_{\text{vap'n}} > 0 \Rightarrow \Delta H_{\text{vap'n}} > \Delta U_{\text{vap'n}} \quad (3.29)$$

Also note that since  $\Delta V_{\text{vap'n}} \gg \Delta V_{\text{fusion}}$ ,  $\Delta H_{\text{fusion}} \approx \Delta U_{\text{fusion}}$ .

$\Delta V_{\text{fusion}} < 0$  for  $H_2O$

- Since  $H$  is a state funct,  $dH$  has an exact differential.

$$dH = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP \rightarrow dH = \left( \frac{\partial H}{\partial T} \right)_P dT = \delta q_P \rightarrow \left( \frac{\partial H}{\partial T} \right)_P = \frac{\delta q_P}{dT} \quad (3.30)$$

$\uparrow$  isobaric process

### 3.4 The Variation of Enthalpy with Temperature at Constant Pressure, $\Delta H_P$ in $H(T,P)$

- The **heat capacity at constant pressure**,  $C_P$ , is defined as

$$C_P \equiv \frac{\delta q_p}{dT} = \left( \frac{\partial H}{\partial T} \right)_P \quad \text{(cf) (3.15) for } C_V \quad (3.32)$$

- In general, a constant pressure process with no change in the phase of the system and no chemical reactions,

$$\Delta H_P = \int_{T_i}^{T_f} C_P(T) dT = n \int_{T_i}^{T_f} C_{P,m}(T) dT \quad \text{(cf) (3.16) for } \Delta U_V \quad (3.33)$$

- Over a limited temperature range,  $C_{P,m}$  can be regarded as a constant and (3.33) simplifies to

$$\Delta H_P = C_P \Delta T = n C_{P,m} \Delta T \quad \text{(cf) (3.17) for } \Delta U_V \quad (3.34)$$



## Example Problem 3.7

A 143.0 g sample of  $C(s)$  in the form of graphite is heated from 300 to 600 K at a constant pressure. Over this temperature range,  $C_{P,m}$  has been determined to be

$$\frac{C_{P,m}}{J / K / mol} = -12.19 + 0.1126 \frac{T}{K} - 1.947 \times 10^{-4} \frac{T^2}{K^2} + 1.919 \times 10^{-7} \frac{T^3}{K^3} - 7.8 \times 10^{-11} \frac{T^4}{K^4}$$

Calculate  $\Delta H$  and  $q_p$ . How large is the relative error in  $\Delta H$  if you neglect the temperature-dependent terms in  $C_{P,m}$  and assume that  $C_{P,m}$  maintains its value at 300 K throughout the temperature interval?

# Solution

From (3.28),  $\Delta H = q_p$ .

$$\begin{aligned}
 \Delta H &= \frac{m}{M} \int_{T_i}^{T_f} C_{P,m}(T) dT \\
 &= \frac{143.0}{12.0} \int_{300}^{600} \left( -12.19 + 0.1126T - 1.947 \times 10^{-4} T^2 + 1.919 \times 10^{-7} T^3 - 7.8 \times 10^{-11} T^4 \right) d\left(\frac{T}{K}\right) \\
 &= \frac{143.0}{12.0} \times \left[ -12.19T + 0.0563T^2 - 6.49 \times 10^{-5} T^3 + 4.798 \times 10^{-8} T^4 - 1.56 \times 10^{-11} T^5 \right]_{300}^{600} \\
 &= 46.85 \text{ kJ}
 \end{aligned}$$

## Solution

If we had assumed  $C_{P,m} = 8.617 \text{ J/mol/K}$ , which is the calculated value at 300 K,

$$\Delta H = \frac{143.0 \text{ g}}{12} \times 8.617 \text{ J/K/mol} \times [600 \text{ K} - 300 \text{ K}] = 30.81 \text{ kJ}$$

The relative error is  $(30.81 - 46.85) \times 100 / 46.85 = -34\%$ .

In this case, it is not reasonable to assume that  $C_{P,m}$  is independent of temperature.

## 3.5 How Are $C_p$ and $C_v$ Related?

- The 1<sup>st</sup> law of TD is written as

$$dU = \delta q - P_{ext}dV = C_v dT + \left( \frac{\partial U}{\partial V} \right)_T dV \quad (3.13)(3.35)$$

- Consider isobaric process. Then since  $\delta q_p = C_p dT$  and  $P = P_{ext}$ , (3.35) becomes

$$dU = C_p dT - P dV = C_v dT + \left( \frac{\partial U}{\partial V} \right)_T dV$$

$$\rightarrow C_p dT = C_v dT + \left( \frac{\partial U}{\partial V} \right)_T dV + P dV \quad (3.36)$$

$$C_p = C_v + \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P \quad (cf) \quad \left( \frac{\partial U}{\partial V} \right)_T + P = T \left( \frac{\partial P}{\partial T} \right)_V \quad (3.19, 5.61)$$

$$= C_v + \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] \left( \frac{\partial V}{\partial T} \right)_P = C_v + T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P \quad (3.37)$$

Very small for L&S

## 3.5 How Are $C_p$ and $C_v$ Related?

- Using  $(\alpha)$  & (3.9), LN 3-10,11 the relationship between  $C_p$  and  $C_v$  is defined as

$$C_p = C_v + TV \frac{\beta^2}{\kappa} \quad \text{or} \quad C_{p,m} = C_{v,m} + TV_m \frac{\beta^2}{\kappa} \quad (cf) \left( \frac{\partial P}{\partial T} \right)_V = \frac{\beta}{\kappa} \quad (\alpha) \quad (3.38)$$

- For id gas from (3.37),  $C_p - C_v = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P = T \left( \frac{nR}{V} \right) \left( \frac{nR}{P} \right) = nR$

$$\text{Therefore, } C_p - C_v = nR \quad \text{or} \quad C_{p,m} - C_{v,m} = R \quad (3.39)$$

- Also in (3.37) since  $\left( \frac{\partial V}{\partial T} \right)_P = v\beta$  is very small for  $L$  or  $S$ , that is

$$C_v \gg \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] \left( \frac{\partial V}{\partial T} \right)_P \quad (3.40)$$

Neglecting the 2<sup>nd</sup> term in (3.37),  $C_p \approx C_v$  for a liquid or a solid.



### 3.6 The Variation of Enthalpy with Pressure at Constant Temperature, $\Delta H_T$ in $H(T,P)$

- Given the definition,  $H=U+PV$

$$\Delta H_T \quad dH = dU + PdV + VdP \quad (3.41)$$

$$\begin{aligned} C_p dT + \left( \frac{\partial H}{\partial P} \right)_T dP &= C_v dT + \left( \frac{\partial U}{\partial V} \right)_T dV + PdV + VdP \\ &= C_v dT + \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] dV + VdP \end{aligned} \quad (3.42)$$

- For isothermal processes  $dT=0$  and divided by  $dP$ , (3.42) becomes

$$\left( \frac{\partial H}{\partial P} \right)_T = \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] \left( \frac{\partial V}{\partial P} \right)_T + V$$

$$\text{Note } \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial T}{\partial V} \right)_P = -1 \text{ (C.R.)} \quad (3.43)$$

$$\text{Note } \left( \frac{\partial T}{\partial P} \right)_V \left( \frac{\partial P}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P = -1 \text{ (C.R.)}$$

- Substituting  $\left( \frac{\partial U}{\partial V} \right)_T + P = T \left( \frac{\partial P}{\partial T} \right)_V$  (3.19) and applying the cyclic rule above, (3.43) becomes

### 3.6 The Variation of Enthalpy with Pressure at Constant Temperature, $\Delta H_T$ in $H(T,P)$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial P}\right)_T + V = V - T\left(\frac{\partial V}{\partial T}\right)_P = V(1 - T\beta) \quad (3.44)$$

- (3.44) can be applied to all systems containing pure substances or mixtures with a fixed composition, provided that no phase changes or chem rx take place,
- In (3.44),  $\beta$  is small for  $L\&S$  and  $(\partial H/\partial P)_T \approx V$ , then from (3.42)

$$dH \approx \underbrace{C_p dT}_{\Delta H_p} + \underbrace{V dP}_{\Delta H_T} \text{ for } L\&S \quad (3.46)$$

- Just as in the case of  $\Delta U$ ,  $\Delta U_V \gg \Delta U_T$ , for  $\Delta H$ ;  $\Delta H_p \gg \Delta H_T$ : The T-dependency is much larger than the P-dependency.

👉 Example Problem 3.9

## Example Problem 3.8: $(\partial H/\partial P)_T$ for id gas

Evaluate  $(\partial H/\partial P)_T$  for an ideal gas.

Solution:

From (3.44) 
$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial P}\right)_T + V,$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial [nRT/V]}{\partial T}\right)_V = \frac{nR}{V} \quad \text{and} \quad \left(\frac{\partial V}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(\frac{nRT}{P}\right)_T = -\frac{nRT}{P^2}$$

for an ideal gas. Therefore,

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{nR}{V}\right)\left(-\frac{nRT}{P^2}\right) + V = -\frac{nRT}{P} \frac{nRT}{nRT} + V = 0$$

In case of id gas,  $H$  is also a function of  $T$  alone!!

or 
$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P = V - \frac{\partial}{\partial T}\left(\frac{nRT}{P}\right)_P = V - \frac{nRT}{P} = 0$$

↑ from *C.R.*

## Example Problem 3.9 : Comparison b/n $\Delta H_T$ and $\Delta H_P$

Calculate the change in enthalpy when 124 *g* of liquid methanol initially at 1.00 *bar* and 298 *K* undergoes a change in state to 2.5 *bar* and 425 *K*. The density of liquid methanol under these conditions is 0.791 *g/cm*<sup>3</sup>, and the  $C_{P,m}$  for liquid methanol is 81.1 *J/K/mol*.

### Solution :

Because  $H$  is a state function, any path b/n initial and final states will give the same  $\Delta H$ . We choose the path methanol (*l*, 1.0 *bar*, 298 *K*)  $\rightarrow$  (*l*, 1.0 *bar*, 425 *K*)  $\rightarrow$  (*l*, 2.5 *bar*, 425 *K*). The first step is isobaric and the second step is isothermal. The total change in  $H$  is from (3.46)

# Solution

$$\Delta H = \Delta H_P + \Delta H_T \approx n \int_{T_i}^{T_f} C_{P,m} dT + \int_{P_i}^{P_f} V dP \approx n C_{P,m} (T_f - T_i) + V (P_f - P_i)$$

$$= 81.1 \text{ J/K/mol} \times \frac{124 \text{ g}}{32.04 \text{ g/mol}} \times (425 \text{ K} - 298 \text{ K})$$

$$+ \frac{124 \text{ g}}{0.791 \text{ g/cm}^3} \times \frac{10^{-6} \text{ m}^3}{\text{cm}^3} \times (2.5 \text{ bar} - 1.0 \text{ bar}) \times \frac{10^5 \text{ Pa}}{\text{bar}}$$

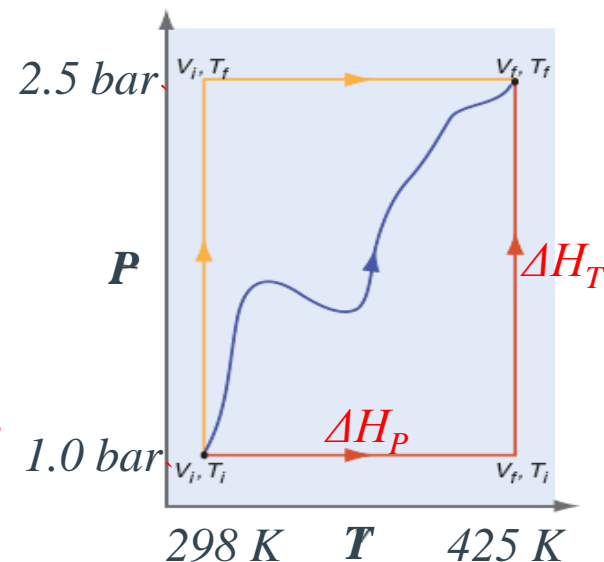
$$= 39.9 \times 10^3 \text{ J} + 23.5 \text{ J} \approx 39.9 \text{ kJ}$$

↑  $\Delta H_P$  0.6%

Typo in p.60 : isothermal ↔ isobaric  
 Section 8 & Section 9 → Section 7 & Section 8

**Q :** Which of  $P$  and  $T$  does more strongly affect  $\Delta H$  ?

**A :**  $T$  does just as for  $\Delta U$ .





## 3.7 The Joule-Thompson Experiment

**Q:** 질소 bombe의 감압밸브가 실수로 열렸을 때 발생하는 냉각현상과 수소 bombe 경우의 가열현상은 무슨 차이 때문에 생길까?

'16/04/04

- The Joule-Thompson experiment allows  $(\partial U/\partial V)_T$  to be measured with a much higher accuracy than in the Joule experiment.

『Joule-Thomson experiment, 1854』

Target :  $\left(\frac{\partial H}{\partial P}\right)_T$  measurement

system :  $N_2$  gas

Brain experiment!!

👉 LN p.3.50 for GWC version

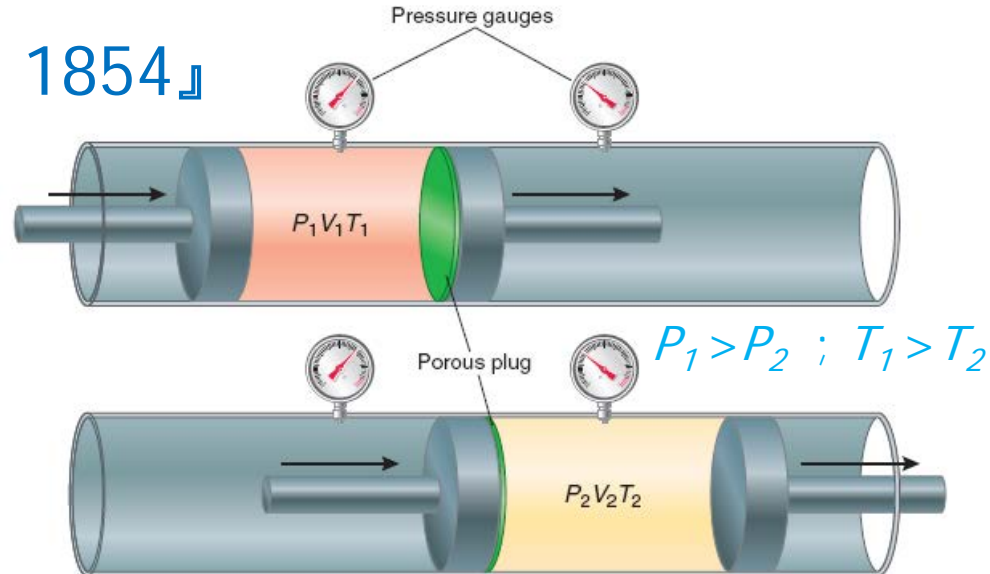


Fig.3.5 Joule-Thomson experiment.

## 3.7 The Joule-Thompson Experiment

$$w = w_{left} + w_{right} = -\int_{V_1}^0 P_1 dV - \int_0^{V_2} P_2 dV = P_1 V_1 - P_2 V_2 \quad ; P_1 > P_2 \quad (3.48)$$

- Because the pipe is insulated,  $q=0$ , and

$$\Delta U = U_2 - U_1 = w = P_1 V_1 - P_2 V_2 \quad (3.49)$$

$$\begin{aligned} du &= dq - Pdv \\ &= 0 + W \end{aligned}$$

- This equation can be rearranged to

$$U_2 + P_2 V_2 = U_1 + P_1 V_1 \quad \text{or} \quad H_2 = H_1 \quad (3.50)$$

**The expansion is *isenthalpic* !!**

- Experimental result :  $dT, dP < 0 \rightarrow \left( \frac{\partial T}{\partial P} \right)_H > 0$  for  $N_2$

## 3.7 The Joule-Thompson Experiment

- The experimentally determined limiting ratio of  $\Delta T$  to  $\Delta P$  at constant enthalpy is known as the **Joule-Thompson coefficient**: unit =  $[K/Pa]$

$$\mu_{J-T} \equiv \lim_{\Delta P \rightarrow 0} \left( \frac{\Delta T}{\Delta P} \right)_H = \left( \frac{\partial T}{\partial P} \right)_H \quad (3.51)$$

~material-dependent property

- For an isenthalpic process,

$$dH = C_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP = 0 \quad (3.52)$$

Dividing thru by  $dP$ , (3.52) becomes

$$C_P \left( \frac{\partial T}{\partial P} \right)_H + \left( \frac{\partial H}{\partial P} \right)_T = 0 \quad \text{giving} \quad \left( \frac{\partial H}{\partial P} \right)_T = -C_P \mu_{J-T} \quad (3.53)$$

$\uparrow$   $J-T$  target

## 3.7 The Joule-Thompson Experiment

- $(\partial U/\partial V)_T$  can be calculated more accurately by use of (3.43),  $C_P$ ,  $\mu_{J-T}$ , and  $\kappa$  as shown in EP3.10 below.

### - EP3.10 -

$$\left(\frac{\partial H}{\partial P}\right)_T = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial P}\right)_T + V \quad (3.43) \quad \rightarrow \quad \left(\frac{\partial U}{\partial V}\right)_T = \frac{\left(\frac{\partial H}{\partial P}\right)_T - V}{\left(\frac{\partial V}{\partial P}\right)_T} - P = \frac{C_P \mu_{J-T} + V}{\kappa V} - P$$

↑ J target

- Values of  $\mu_{J-T}$  at 273 K and 1 atm are shown below.

Gas	$\mu_{J-T}$ (K/MPa)
Ar	3.66
C <sub>6</sub> H <sub>14</sub>	-0.39
CH <sub>4</sub>	4.38
CO <sub>2</sub>	10.9
H <sub>2</sub>	-0.34
He	-0.62
N <sub>2</sub>	2.15
Ne	-0.30
NH <sub>3</sub>	28.2
O <sub>2</sub>	2.69

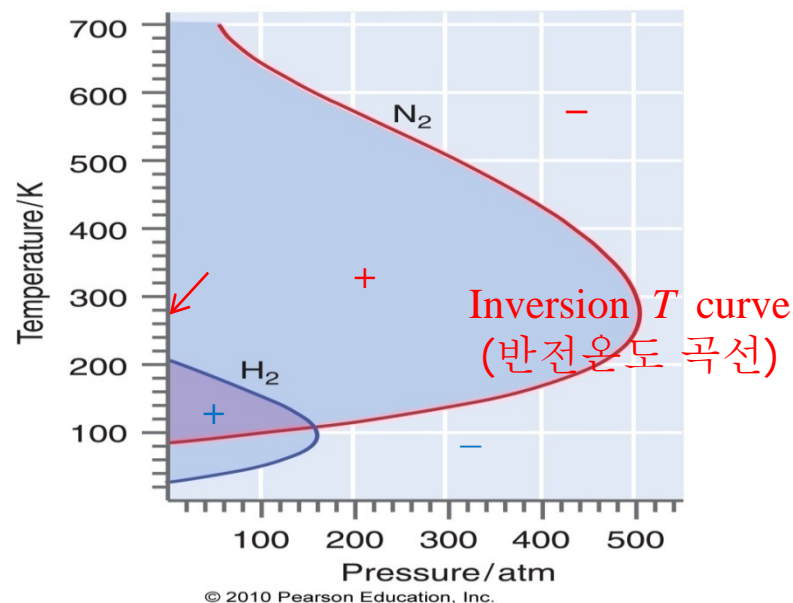


Fig.3.6  $\mu_{J-T}$  of N<sub>2</sub> and H<sub>2</sub>.

## 3.7 The Joule-Thompson Experiment

Ref. GWC, "PC", 3<sup>rd</sup> ed., A-W, pp. 124-125

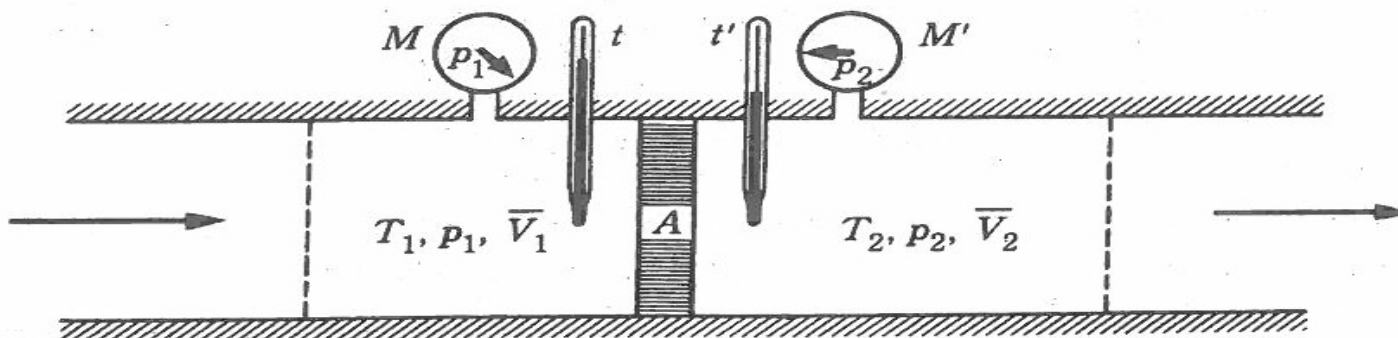


Figure 7.9 The Joule–Thomson experiment.

Consider the passage of one mole of gas through the obstruction. The volume on the left decreases by the molar volume  $\bar{V}_1$ ; since the gas is pushed by the gas behind it, which exerts a pressure  $p_1$ , the work produced is

$$W_{\text{left}} = -\int_{\bar{V}_1}^0 p_1 dV$$

The volume on the right increases by the molar volume  $\bar{V}_2$ ; the gas coming through must push the gas ahead of it, which exerts an opposing pressure,  $p_2$ . The work produced is

$$W_{\text{right}} = -\int_0^{\bar{V}_2} p_2 dV$$

The net work produced is the sum of these two amounts

$$W = -\int_{\bar{V}_1}^0 p_1 dV - \int_0^{\bar{V}_2} p_2 dV = p_1(\bar{V}_1) - p_2\bar{V}_2 = p_1\bar{V}_1 - p_2\bar{V}_2$$



## Example Problem 3.11

Using (3.43), show that  $\mu_{J-T}=0$  for an ideal gas.

$$\left(\frac{\partial H}{\partial P}\right)_T = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial P}\right)_T + V \quad (3.43)$$

이상기체는  $imf=0$  이므로  $P$ 의 증가나 감소로 분자간 거리가 바뀌는 데 에너지가 필요치 않음.

Solution :

$$\begin{aligned} \mu_{J-T} &= -\frac{1}{C_P} \left(\frac{\partial H}{\partial P}\right)_T = -\frac{1}{C_P} \left[ \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T + P \left(\frac{\partial V}{\partial P}\right)_T + V \right] \\ &= -\frac{1}{C_P} \left[ 0 + P \left(\frac{\partial V}{\partial P}\right)_T + V \right] \\ &= -\frac{1}{C_P} \left[ P \left( \frac{\partial [nRT/P]}{\partial P} \right)_T + V \right] = -\frac{1}{C_P} \left[ -\frac{nRT}{P} + V \right] = 0 \end{aligned}$$

$(\partial u / \partial v)_T = 0$  for  
ideal gas, slide-21

A: When  $\mu_{J-T} > 0$ ,  $T \downarrow$  on isenthalpic expansion and *vice versa*.

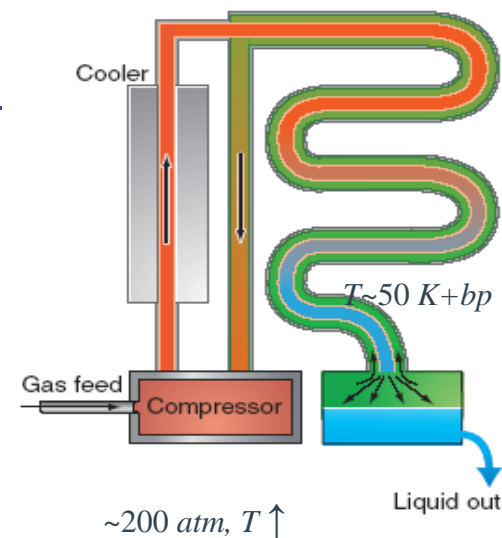
## 3.8 Liquefying Gases Using an Isenthalpic expansion

isenthalpic expansion = J-T expansion = adiabatic expansion

Heat is extracted from the pre-pressurized gas in the cooler exiting from the compressor in Fig.3.7.

It is further cooled in the countercurrent(향류) heat exchanger within  $\sim 50\text{ K}$  of the boiling point before expanding through a nozzle.

At the exit of the heat exchanger, the gas undergoes a Joule-Thomson expansion (describes the temperature change of a real gas or liquid when it is forced through a valve or porous plug while keeping it insulated so that no heat is exchanged). Because its temperature falls below boiling point, liquefaction occurs.



## <인공 눈 형성 원리>

원통처럼 생긴 제설기에는 비슷하게 생긴 두 종류의 노즐이 달려 있다. 인공 눈의 핵을 만드는 노즐에서는, 미세한 물방울이 섞여 있는 고압의 공기(약 50기압)를  $J-T$  팽창노즐을 통해 뿌려준다. 이때 공기가 급격하게 단열 팽창하며 온도가 뚝 떨어져서 물방울은 얼음 알갱이가 되어 눈 핵, 즉 인공 눈의 씨앗이 만들어진다.

다른 노즐은 그냥 분무기처럼 미세한 물방울을 분출하는데, 1500 rpm으로 회전하는 날개에 의해 크기가 약  $5\sim 50\ \mu m$ 인 이 미세한 물방울들이 눈의 씨앗에 순식간에 달라붙어 인공 눈이 되는 것이다.

결국 두 노즐에서 나온 눈의 씨앗과 물방울이 공중에서 서로 잘 만나도록 하는 것이 제설기 설계의 핵심기술이다.

인공 눈은 자연 눈에 비해 상대적으로 습도가 높아 잘 뭉쳐지고 단단하므로 마찰력이 커서, 스키어들이 활강이나 회전할 때 그 마찰력으로 인해 녹은 물이 윤활유 역할을 해주므로 **skiing**에 더욱 적합하다.

The cylinder-like snow thrower has two types of nozzles that look alike. In the nozzle, high-pressure air (about 50 atm) mixed with fine droplets is sprayed through the J-T expansion nozzle. At this time, the air expands suddenly adiabatically **(without transfer of heat)**, and the temperature drops, so the water drops become ice granules, that is, the artificial snow, are made.

The other nozzles just spray fine droplets like a sprayer, and these fine droplets, about 5 to 50  $\mu\text{m}$  in size.

In the end, it is the core technology of the snowplow design that the seeds and droplets of snow from the two nozzles meet each other in the air.

The artificial snow is more suitable for skiing because it is relatively high in humidity compared to natural snow, so it is well-formed and hard so that the friction is strong and the water melted due to the frictional force when the skier slides or turns.