CY11001
Spring 2018

- Heat Capacity
- Enthalpy

Department of Chemistry
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Kharagpur

Heat Transactions and Heat Capacity:

In general change in the internal energy of a closed system is given by

$$dU = dq + dw_{\text{exp}} + dw_{\text{add}}$$

- For $dV = 0$; $dw_{\text{exp}} = 0$ and if $dw_{\text{add}} = 0$,   then

$dU = dq$ (constant volume, no additional work) $= dq_V$

For a measurable change $\Delta U = q_V$

The measurement of internal energy change
- *Adiabatic bomb calorimeter*

- **heat capacity**, C, the ratio of the heat supplied to the temperature rise it causes. $C = dq/dT$; $C = q/\Delta T$

- **heat capacity at constant volume,** $C_V = (\partial U / \partial T)_V$

- **molar heat capacity,** the heat capacity divided by the amount of substance, $C_{\text{m}} = C/n$.

- **specific heat capacity,** the heat capacity divided by the mass, $C_{\text{s}} = C/m$

Resistance thermometer

Oxygen inlet

Firing leads

Water

Sample

Heater
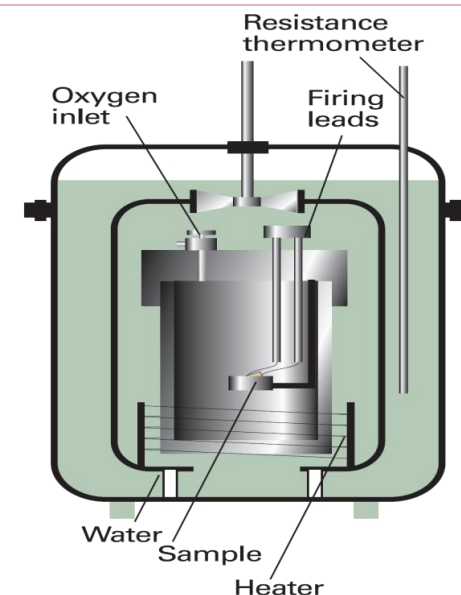
Heat Capacity at Constant Pressure:

$$dU = dq + dw_{\exp} + dw_{\text{add}}$$

For $dV \neq 0$; $dw_{\exp} \neq 0$ Even if $dw_{\text{add}} = 0$, $dU \neq dq$

Define $H = U + pV$

$dH = dU + pdV + Vdp = dU - w$ (at const p) $= dq_p$

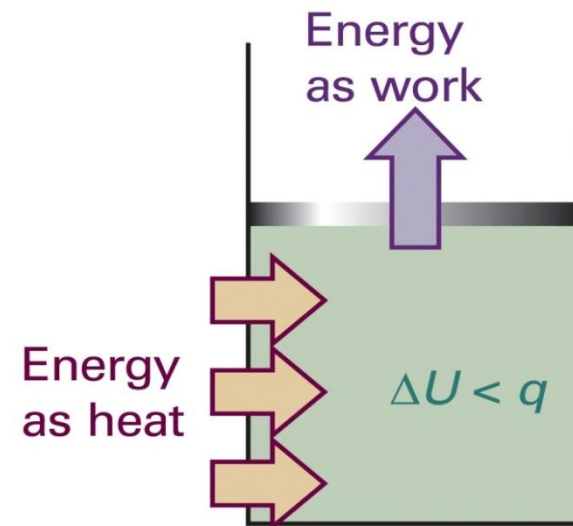**heat capacity at constant pressure,** $C_p = (\partial H / \partial T)_p$

Energy as work

Energy as heat $\Delta U < q$

Figure 2-12
Atkins Physical Chemistry, Eighth Edition
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The measurement of enthalpic change
- *isobaric calorimeter*
- *differential scanning calorimeter*
- *adiabatic flame calorimeter*

For ideal gas; **relation between ΔU and ΔH,**

$\Delta H = \Delta U + \Delta n_g RT$.

Show that for a perfect gas, $C_p - C_V = nR$

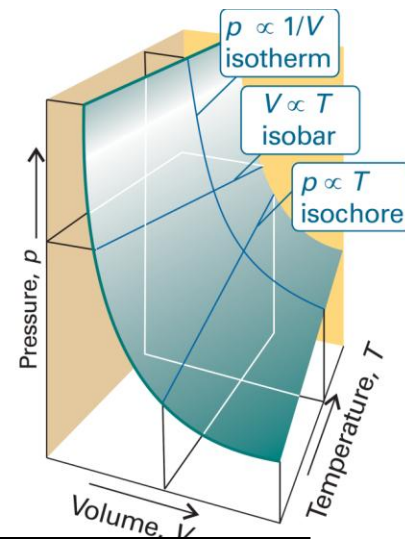(home work)

- For most cases, $C_p > C_V$

Partial differentiation:

Consider a function of two variables ➜ z = *f(x,y)*

A **partial derivative** of one of the variables: the rate of change of the function *wrt* that variable with all other variables kept fixed.

Example: For *z = f(x,y),*

$$\left(\frac{\partial z}{\partial x}\right)_y = \lim_{\Delta x \to 0} \frac{f(x + \Delta x, y) - f(x, y)}{\Delta x}$$

$$\left(\frac{\partial z}{\partial y}\right)_x = \lim_{\Delta y \to 0} \frac{f(x, y + \Delta y) - f(x, y)}{\Delta y}$$

Total differential of *z(x,y)*:

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

$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$$

Clairaut's theorem

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

Cyclic Rule

Variation of internal energy with T and V

$$U = f(V,T) \qquad U = f(p,T) \qquad U = f(p,V)$$

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

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$$

Internal pressure

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Heat capacity

$$dU = \pi_T dV + C_V dT$$

Special case: Ideal gas

Constant V process

$$dU_V = C_V dT$$

Constant T process

$$dU_T = \pi_T dV$$

For ideal gas

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad \left(\frac{\partial U}{\partial p}\right)_T = 0$$

$$dU = C_V dT \quad \underline{\text{for ideal gas}}$$

Internal energy, U

Repulsions dominant

$\pi_T < 0$

Perfect gas
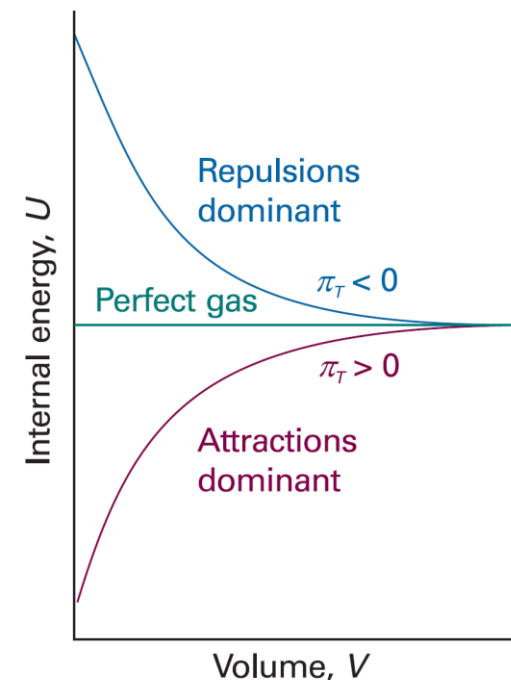
$\pi_T > 0$

Attractions dominant

Volume, V

Fig. 2.25 For a perfect gas, the internal energy is independent of the volume (at constant temperature). If attractions are dominant in a real gas, the internal energy increases with volume because the molecules become farther apart on average. If repulsions are dominant, the internal energy decreases as the gas expands.
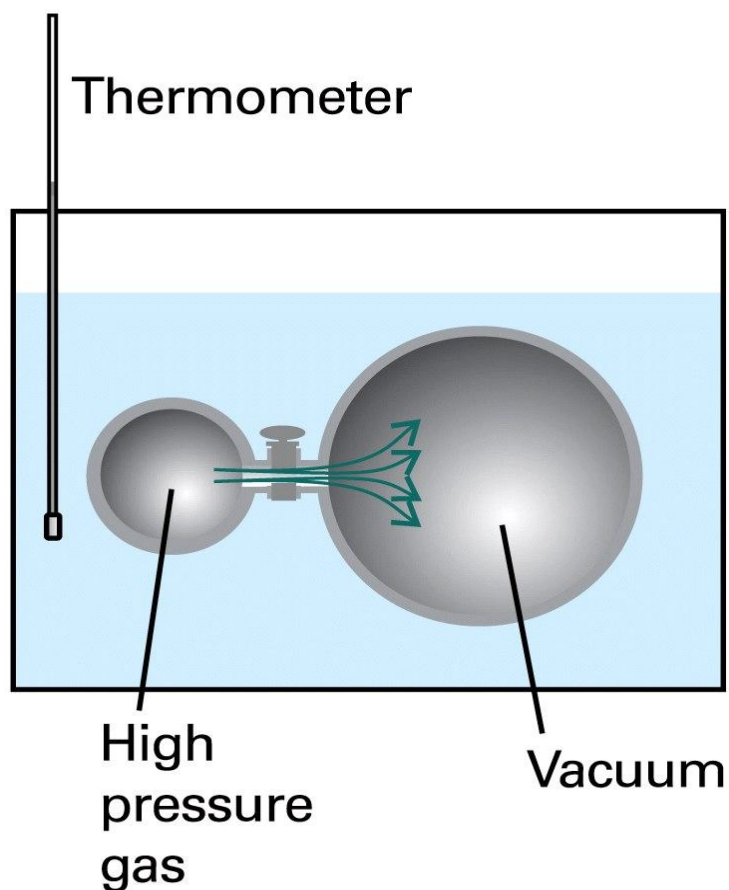
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Joule's Experiment (1843)

Thermometer

High pressure gas

Vacuum

Figure 2-26
Atkins Physical Chemistry, Eighth Edition
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Purpose is to determine π_T, $\boxed{\left(\dfrac{\partial U}{\partial V}\right)_T}$

whether or not gases cool on expansion, and if so how much.

$$U = f(V,T); \ \ dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

- In this experiment, observed $dT = 0$
- Heat change, q, for the system (gas) $= 0$
- no work done for free expansion, $w = 0$
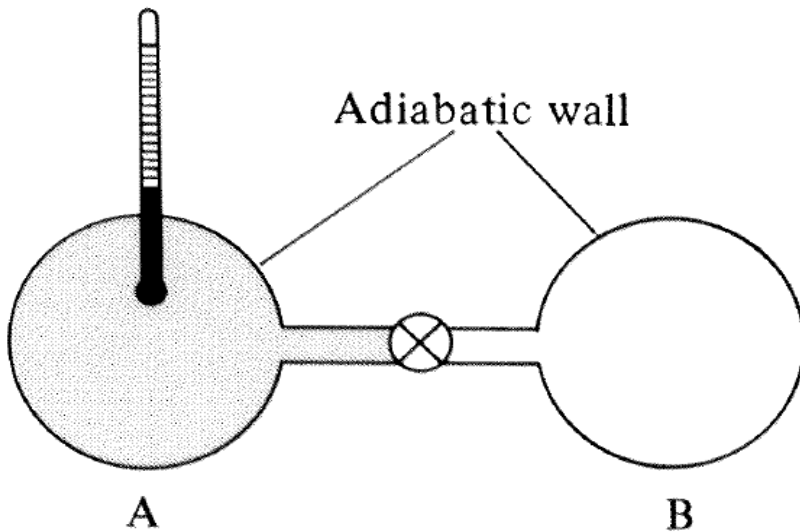
hence $dU = 0$, and,

as $dV \neq 0$, $\boxed{\left(\dfrac{\partial U}{\partial V}\right)_T = 0}$

Actually this is only valid for ideal gas

In reality, $dT \neq 0$, Joule's apparatus was not sensitive to find out the small value of dT

Keyes-Sears modification (1924)

Adiabatic wall

A   B

- Heat change, q, for the system (gas) = 0
- no work done for free expansion, w = 0

hence dU = 0,

Constant-energy process, U constant

$$\left(\frac{\partial T}{\partial V}\right)_U = \mu_J \qquad \approx \frac{\Delta T}{\Delta V}$$ Joule Coefficient, μ_J

$$\left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U = -1$$

$$dU = \pi_T dV + C_V dT$$

$$dU = -C_V \mu_J dV + C_V dT$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U = -C_V \mu_J$$

Partial derivatives of *p*, *V_m*, and *T* with respect to each other:

$$V_m = f(p,T); \quad p = f(V_m, T); \quad T = f(p, V_m)$$

$$dT = \left(\frac{\partial T}{\partial p}\right)_{V_m} dp + \left(\frac{\partial T}{\partial V_m}\right)_p dV_m$$

$$dp = \left(\frac{\partial p}{\partial T}\right)_{V_m} dT + \left(\frac{\partial p}{\partial V_m}\right)_T dV_m$$

$$dV_m = \left(\frac{\partial V_m}{\partial T}\right)_p dT + \left(\frac{\partial V_m}{\partial p}\right)_T dp$$

$$\left(\frac{\partial p}{\partial V_m}\right)_T \left(\frac{\partial V_m}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_{V_m} = -1$$

$$\frac{\partial^2 T}{\partial p \partial V_m} = \frac{\partial^2 T}{\partial V_m \partial p} \left(= \frac{1}{R} \text{ for ideal gas} \right)$$

$$\alpha(T, p) = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_p \qquad \kappa(T, p) = -\frac{1}{V_m}\left(\frac{\partial V_m}{\partial p}\right)_T$$

Expansion coefficient   Isothermal compressibility

$$\left(\frac{\partial p}{\partial T}\right)_{V_m} = -\frac{\left(\partial V_m / \partial T\right)_p}{\left(\partial V_m / \partial p\right)_T} = \frac{\alpha(T, p)}{\kappa(T, p)}$$

- How fast the (fraction of) volume increases with temperature and decreases with pressure

- For ideal gas, $\alpha = 1/T$ and $\kappa = 1/p$

FIRST YEAR TIME TABLE FOR SECTION 15
Strength: 82
SPRING SEMESTER 2017 – 2018

Period	1	2	3	4	5		6	7	8	9
Time / Day	8:00 AM - 8:55 AM	9:00 AM - 9:55 AM	10:00 AM - 10:55 AM	11:00 AM - 11:55 AM	12:00 Noon - 12:55 PM		2:00 PM - 2:55 PM	3:00 PM - 3:55 PM	4:00 PM - 4:55 PM	5:00 PM - 5:55 PM
MON		CHEMISTRY LAB (In Chemistry Department)				L U N C H	INTRO. TO MANUF. PROCESSES LAB (In Mechanical Engineering Department)			
TUE		ELECTRICAL TECHNOLOGY LAB (In Sir J C Bose Laboratory Complex)					HS LAB (In Language Lab, Sir J C Bose Laboratory Complex)			
WED			HS NR221	CY NR221	EE NR 221	H O U R		CY(T) NC241,NC242	MA(T) NC241,NC242	
THU				EE NR221	CY NR221			MA V2		
FRI	CY NR221	EE NR22		HS NR221				MA V2		
SAT	EAA									

NR222

11 Jan and 18 Jan
10 am at NR222

FIRST YEAR TIME TABLE FOR SECTION 16
Strength: 80
SPRING SEMESTER 2017 – 2018

Period	1	2	3	4	5		6	7	8	9
Time / Day	8:00 AM - 8:55 AM	9:00 AM - 9:55 AM	10:00 AM - 10:55 AM	11:00 AM - 11:55 AM	12:00 Noon - 12:55 PM		2:00 PM - 2:55 PM	3:00 PM - 3:55 PM	4:00 PM - 4:55 PM	5:00 PM - 5:55 PM
MON		HS LAB (In Language Lab, Sir J C Bose Laboratory Complex)				L U N C H	ELECTRICAL TECHNOLOGY LAB (In Sir J C Bose Laboratory Complex)			
TUE		CHEMISTRY LAB (In Chemistry Department)					INTRO. TO MANUF. PROCESSES LAB (In Mechanical Engineering Department)			
WED			HS NR221	CY NR221	EE NR221	H O U R		CY(T) NC243,NC244	MA(T) NC243,NC244	
THU				EE NR221	CY NR221			MA V2		
FRI	CY NR221	EE NR 221		HS NR221				MA V2		
SAT	EAA									