Lecture 5

Thermodynamic Response Functions

Measuring the Change in Internal Energy

$$\Delta U = q + w$$

Constant volume process

Adiabatic process

$$\Delta U = q_V$$
$$(w = 0)$$

$$\Delta U = w$$
$$(q = 0)$$

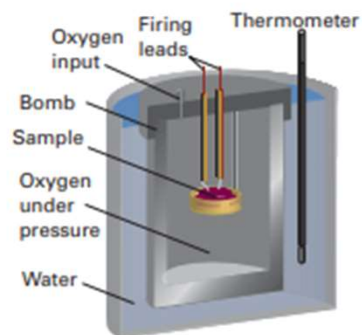Estimate q_v with a calorimeter

Estimate w as PV work

Fig. 2.9 A constant-volume bomb calorimeter. The 'bomb' is the central vessel, which is strong enough to withstand high pressures. The calorimeter (for which the heat capacity must be known) is the entire assembly shown here. To ensure adiabaticity, the calorimeter is immersed in a water bath with a temperature continuously readjusted to that of the calorimeter at each stage of the combustion.

(Labels on figure: Oxygen input, Firing leads, Thermometer, Bomb, Sample, Oxygen under pressure, Water)

The change in temperature, ΔT, of the calorimeter is proportional to the energy that the reaction releases or absorbs as heat. Therefore, by measuring ΔT we can determine q_V and hence find ΔU. The conversion of ΔT to q_V is best achieved by calibrating the calorimeter using a process of known energy output and determining the calorimeter constant, the constant C in the relation

$$q = C\Delta T$$

A note on heat-capacity and specific heat (capacity) (Response Function)

Heat capacities are extensive properties: 100 g of water, for instance, has 100 times the heat capacity of 1 g of water (and therefore requires 100 times the energy as heat to bring about the same rise in temperature). The **molar heat capacity at constant volume**, $C_{V,m} = C_V/n$, is the heat capacity per mole of substance, and is an intensive property (all molar quantities are intensive). Typical values of $C_{V,m}$ for polyatomic gases are close to 25 J K^{-1} mol^{-1}. For certain applications it is useful to know the **specific heat capacity** (more informally, the 'specific heat') of a substance, which is the heat capacity of the sample divided by the mass, usually in grams: $C_{V,s} = C_V/m$. The specific heat capacity of water at room temperature is close to 4.2 J K^{-1} g^{-1}. In general, heat capacities depend on the temperature and decrease at low temperatures. However, over small ranges of temperature at and above room temperature, the variation is quite small and for approximate calculations heat capacities can be treated as almost independent of temperature.

Variation of Internal Energy U with Volume

- Variation with volume at constant temperature $\left(\frac{\partial U}{\partial V}\right)_{T,N}$

James Prescott Joule

Joule's experiment

Isothermal expansion of an ideal gas **against zero pressure**

Observation: $dT = 0$

$\delta w = 0; \quad \delta q = 0$

Repulsions dominant, $\pi_T < 0$

Perfect gas

Attractions dominant, $\pi_T > 0$

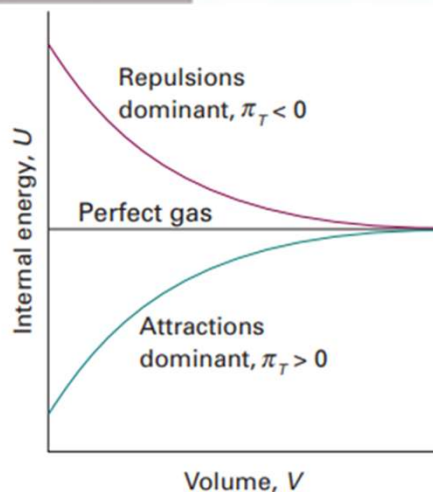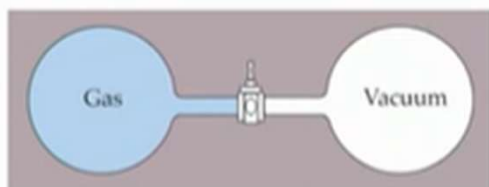Internal energy, U

Volume, V

Fig. 2.24 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.

$U = U(T, V_,)$

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

Response function :- $\boxed{C_v = \left(\frac{\partial u}{\partial T}\right)_V}$ $\boxed{\pi_T = \left(\frac{\partial u}{\partial V}\right)_T}$

Specific heat at const. volume

Internal Pressure

$du = C_v \, dT + \pi_T \, dV$

$\Delta u = C_v \, \Delta T + \pi_T \, \Delta V$

Now, as $U = U(T, V)$

Following cyclic rule, we can write,

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

Hence, $\left(\frac{\partial u}{\partial V}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_u \left(\frac{\partial u}{\partial T}\right)_V$

$\pi_T = -\mu_J C_v$

$\boxed{\mu_J = \left(\frac{\partial T}{\partial V}\right)_u} \implies$ Joule's coefficient

Response Functions

$$\left(\frac{\partial U}{\partial T}\right)_P = \pi_T \left(\frac{\partial V}{\partial T}\right)_P + C_V$$

It is usually sensible in thermodynamics to inspect the output of a manipulation like this to see if it contains any recognizable physical quantity. The partial derivative on the right in this expression is the slope of the plot of volume against temperature (at constant pressure). This property is normally tabulated as the **expansion coefficient**, α, of a substance, which is defined as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

> Definition of the expansion coefficient [2.42]

and physically is the fractional change in volume that accompanies a rise in temperature. A large value of α means that the volume of the sample responds strongly to changes in temperature. Table 2.9 lists some experimental values of α. For future reference, it also lists the **isothermal compressibility**, κ_T (kappa), which is defined as

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

> Definition of the isothermal compressibility [2.43]

Table 2.9* Expansion coefficients (α) and isothermal compressibilities (κ_T) at 298 K

	$\alpha/(10^{-4}\,K^{-1})$	$\kappa_T/(10^{-6}\,bar^{-1})$
Benzene	12.4	90.9
Diamond	0.030	0.185
Lead	0.861	2.18
Water	2.1	49.0

* More values are given in the *Data section*.

The isothermal compressibility is a measure of the fractional change in volume when the pressure is increased by a small amount; the negative sign in the definition ensures that the compressibility is a positive quantity, because an increase of pressure, implying a positive dp, brings about a reduction of volume, a negative dV.

Example 2.8 *Calculating the expansion coefficient of a gas*

Derive an expression for the expansion coefficient of a perfect gas.

Method The expansion coefficient is defined in eqn 2.42. To use this expression, substitute the expression for V in terms of T obtained from the equation of state for the gas. As implied by the subscript in eqn 2.42, the pressure, p, is treated as a constant.

Answer Because $pV = nRT$, we can write

$$\alpha = \frac{1}{V}\left(\frac{\partial(nRT/p)}{\partial T}\right)_p = \frac{1}{V} \times \frac{nR}{p}\frac{dT}{dT} = \frac{nR}{pV} = \frac{1}{T}$$
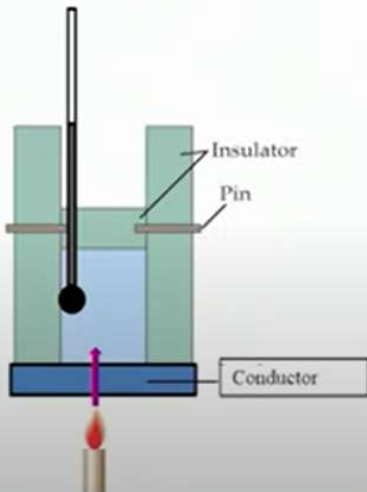
The higher the temperature, the less responsive is the volume of a perfect gas to a change in temperature.

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Self-test 2.9 Derive an expression for the isothermal compressibility of a perfect gas.
$$[\kappa_T = 1/p]$$

Introducing Enthalpy
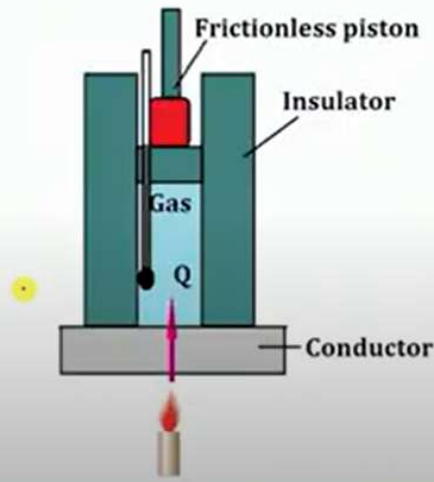
Heating at constant volume

- $\Delta U = q_V$

Schematic diagram

- Insulator
- Pin
- Conductor

$$q_V = Q = m\,C_V\,\Delta T$$

Heating at constant pressure

Schematic diagram

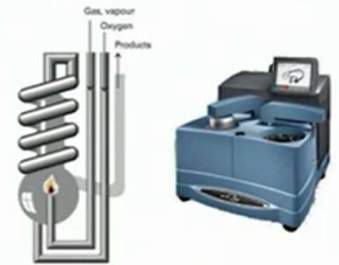- Frictionless piston
- Insulator
- Gas
- Q
- Conductor

$$q_p = Q = m\,C_P\,\Delta T$$

Enthalpy and heat

- $H = U + pV$ and $\Delta H = Q_p$

Enthalpy changes are measured using

- isobaric calorimeter
- differential scanning calorimeter
- adiabatic flame calorimeter

- **Properties** of H:

✓ state function, $\Delta H = H_2 - H_1$ for change in state from 1 to 2

✓ **exact differential**
$$dH = d(U + pV) = dU + pdV + Vdp$$

✓ For constant pressure processes,
$$dp = 0 \quad \Rightarrow \quad dH = dU + pdV = \eth q_p \quad \text{(Using 1}^{st}\text{ law)}$$

✓ **For finite isobaric process**
$$\int_1^2 dH = \Delta H = H_2 - H_1 = \int_1^2 \eth q_p = Q_p$$

$$\Delta H = Q_p$$

Variation of Enthalpy with Temperature & Pressure

By definition, $\quad dH = dU + d(pV)$

For an ideal gas, $\quad pV = nRT$

$$\therefore dH = dU + Rd(nT)$$

For an **ideal gas** undergoing **isothermal change in state** (e.g. a gas phase chemical reaction at constant T),

$$dH = dU + RTd(n) \Rightarrow \boxed{\Delta H = \Delta U + (\Delta n)RT}$$

In general, **for a closed system**

$$H = H(p, T)$$

$$dH = C_p\, dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

Variation with temperature at constant pressure

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad dH_p = C_p\, dT \qquad \Delta H_p = Q_p = C_p\, \Delta T$$

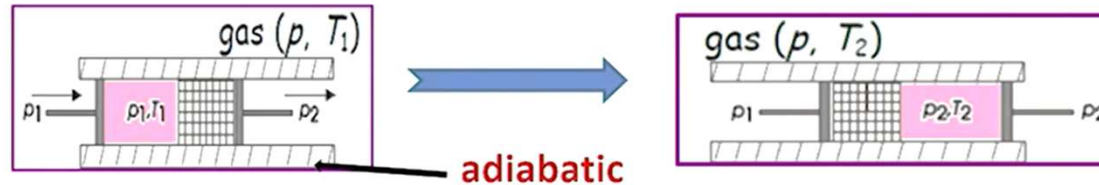Variation with pressure at constant temperature

$$H = H(p, T)$$

$$\therefore \left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_p = -1$$

$$\therefore \left(\frac{\partial H}{\partial p}\right)_T = -\left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial H}{\partial T}\right)_p = -\mu_{JT}\, C_p$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H$$

Jule Thompson Coefficient

adiabatic

For this experiment, $q = 0 \Rightarrow \Delta U = U_2 - U_1 = w$

Observation of the Joule–Thomson effect: The analysis of the Joule–Thomson coefficient is central to the technological problems associated with the liquefaction of gases. We need to be able to interpret it physically and to measure it. As shown in the following Justification, the cunning required to impose the constraint of constant enthalpy, so that the process is isenthalpic, was supplied by Joule and William Thomson (later Lord Kelvin). They let a gas expand through a porous barrier from one constant pressure to another and monitored the difference of temperature that arose from the expansion (Fig. 2.26). The whole apparatus was insulated so that the process was adiabatic. They observed a lower temperature on the low pressure side, the difference in temperature being proportional to the pressure difference they maintained. This cooling by isenthalpic expansion is now called the Joule–Thomson effect.

For this experiment, $q = 0 \Rightarrow \Delta U = U_2 - U_1 = w$

$$w = -p_1(0 - V_1) - p_2(V_2 - 0) = p_1 V_1 - p_2 V_2$$

Thus, $U_2 - U_1 = p_1 V_1 - p_2 V_2 \Rightarrow U_2 + p_2 V_2 = U_1 + p_1 V_1$

$$\therefore \; H_2 = H_1$$

Isenthalpic expansion of a gas from a region of constant high pressure to a region of constant low pressure through a porous plug

$$\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H \approx \frac{\Delta T}{\Delta p} \quad \text{under isenthalpic condition}$$

Jule Thompson Effect and Inversion Temperature

The <u>inversion temperature</u> of a gas is the temperature below which the gas exhibits the Joule-Thomson effect (cooling upon expansion at constant enthalpy) and above which it heats up upon expansion.
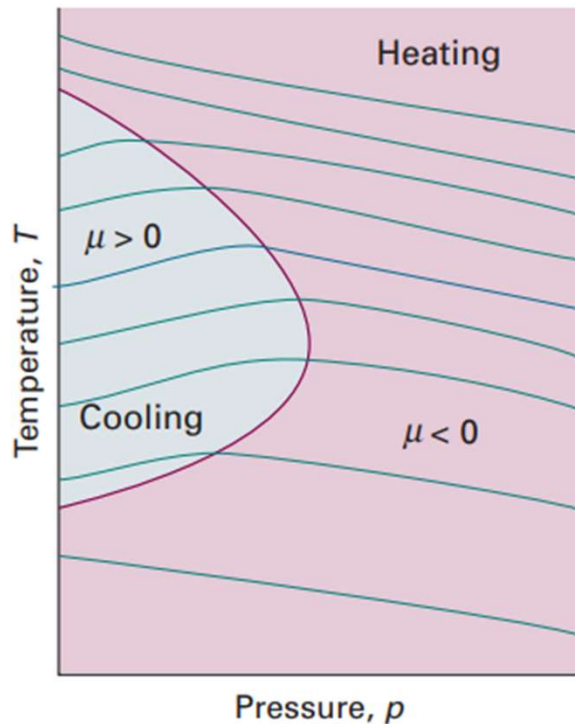
Fig. 2.30 The sign of the Joule–Thomson coefficient, μ, depends on the conditions. Inside the boundary, the blue area, it is positive and outside it is negative. The temperature corresponding to the boundary at a given pressure is the 'inversion temperature' of the gas at that pressure. For a given pressure, the temperature must be below a certain value if cooling is required but, if it becomes too low, the boundary is crossed again and heating occurs. Reduction of pressure under adiabatic conditions moves the system along one of the isenthalps, or curves of constant enthalpy. The inversion temperature curve runs through the points of the isenthalps where their slope changes from negative to positive.

Gas	Inversion temperature
He	40 K
H_2	202 K
Ne	231 K
N_2	621 K
Air	673 K
O_2	764 K
CO_2	1500K

N_2 and O_2 will cool upon expansion at room temperature, but He, H_2 and Ne will warm upon expansion at room temperature.

Temperature, T

Heating

$\mu > 0$

Cooling

$\mu < 0$

Pressure, p

Homework ➡ For a van der Waals gas, $\mu_{JT} = \dfrac{1}{C_p}\left(\dfrac{2a}{RT} - b\right)$

Understand the molecular explanation as taught in the class

Thermodynamic Response Functions

These are **measurable quantities** that can be obtained from experiments involving variation of p, V, T of closed systems

Response function	Definition
Specific heat at constant volume	$C_V = \left(\dfrac{\partial U}{\partial T}\right)_V$
Specific heat at constant pressure	$C_p = \left(\dfrac{\partial U}{\partial T}\right)_p$
Isobaric expansion coefficient	$\alpha = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_p$
Joule coefficient	$\mu_J = \left(\dfrac{\partial T}{\partial V}\right)_U$
Joule Thomson coefficient	$\mu_{JT} = \left(\dfrac{\partial T}{\partial p}\right)_H$

Expression of $\bar{c}_p - \bar{c}_v$:

We have by definition, $\quad \bar{c}_p - \bar{c}_v = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$

But, $H = U + PV$ or $\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$

Hence, $\bar{c}_p - \bar{c}_v = \left(\frac{\partial U}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V + P\left(\frac{\partial V}{\partial T}\right)_P$

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

dividing by dT at constant 'P' —

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

or, $\left(\frac{\partial U}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$

Putting the value, $\bar{c}_p - \bar{c}_v = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$

But, thermodynamic equation of state is, $\boxed{P + \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V}$

Hence, $\boxed{\bar{c}_p - \bar{c}_v = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P}$

This is the general expression of $\bar{c}_p - \bar{c}_v$ for any system, ideal or real and is valid also for condensed system.

(a) $\overline{C_P} - \overline{C_V}$ for **Ideal Gas :** The equation of state is, $PV = nRT$

& for 1 mole, $PV = RT$

Hence, $\left(\dfrac{\partial P}{\partial T}\right)_V = \dfrac{R}{V}$ & $\left(\dfrac{\partial V}{\partial T}\right)_P = \dfrac{R}{P}$ so, $\boxed{\overline{C_P} - \overline{C_V} = R}$ for ideal gas

(c) $\overline{C_P} - \overline{C_V}$ for **VDW Gas :** The equation of state for 1 mole is —

$$\left(P + \dfrac{a}{V^2}\right)(V - b) = RT$$

or, $P = \dfrac{RT}{V - b} - \dfrac{a}{V^2}$ or, $\left(\dfrac{\partial P}{\partial T}\right)_V = R/(V-b)$

Again, the equation —

$PV - Pb + \dfrac{a}{V} = RT$ or, $P\left(\dfrac{\partial V}{\partial T}\right)_P - \dfrac{a}{V^2}\left(\dfrac{\partial V}{\partial T}\right)_P = R$ or, $\left(\dfrac{\partial V}{\partial T}\right)_P = \dfrac{R}{P - \frac{a}{V^2}}$

Therefore, $\overline{C_P} - \overline{C_V} = T\left(\dfrac{\partial P}{\partial T}\right)_V \left(\dfrac{\partial V}{\partial T}\right)_P$

$= T \times \dfrac{R}{V - b} \times \dfrac{R}{P - a/V^2} = \dfrac{R^2 T}{(V - b)\left(P + \dfrac{a}{V^2} - \dfrac{2a}{V^2}\right)}$

$= \dfrac{R^2 T}{(V - b)\left(\dfrac{RT}{V - b} - \dfrac{2a}{V^2}\right)} = \dfrac{R^2 T}{(V - b) \times \dfrac{RT}{V - b}\left(1 - \dfrac{2a(V - b)}{V^2 RT}\right)}$

$= \dfrac{R}{\left(1 - \dfrac{2a}{RTV}\right)} = R\left(1 - \dfrac{2a}{RTV}\right)^{-1} = R\left(1 + \dfrac{2a}{RTV}\right) = \left(R + \dfrac{2a}{TV}\right)$ Putting $V = \dfrac{RT}{P}$

We have, $\boxed{\overline{C_P} - \overline{C_V} = R + \dfrac{2aP}{RT^2}}$ This shows that for VDW Gas, $\overline{C_P} - \overline{C_V}$ is greater than R.

(d) $\overline{C}_p - \overline{C}_V$ in terms of α and β:

By definition, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ and $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

Therefore, $\overline{C}_p - \overline{C}_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = T \times \frac{\alpha}{\beta} \times \alpha V$

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

Since, $\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1$ [According to cyclic Rule]

So, $$\boxed{\overline{C}_p - \overline{C}_V = \frac{\alpha^2 T V}{\beta}}$$