# JOULE EXPERIMENT

A schematic diagram of the apparatus used by Joule in an attempt to measure the change in internal energy when a gas expands isothermally (gas expands into a vacuum).

The heat absorbed by the gas is proportional to the change in temperature of the bath.

 $\lim p_1 \to 0, \Delta T_{bath} = 0$ 

 $p_1$  is the pressure of the gas &

it expands into the bulb at  $p_2 = 0$ 

$$\Delta U = q + w$$

$$w = 0 \& q = C_V \Delta T$$

when a low pressure gas (ideal gas)

is expanded it does so without a change in internal energy, U.

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

From Joule's experiment,

dU = 0 & dT = 0

hence 
$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$
 for an ideal gas.

#### Conclusion:

The internal energy of the gas is independent of the volume.

i.e., U = f(T) only for an ideal gas.



# Joule Thomson Experimentt

A diagram of the apparatus used for measuring the Joule-Thomson effect is shown here. The gas expands through the porous barrier, which acts as a valve, and the whole apparatus is thermally insulated. This arrangement corresponds to an isenthalpic expansion (expansion at constant enthalpy). Whether the expansion results in a heating or a cooling of the gas depends on the conditions.



#### Joule Thomson expansion.

A gas at initial temperature and pressure  $T_i$ ,  $p_i$ is expanded at constant pressure through a small valve or what is called a porous plug under adiabatic condition [system insulated so that no heat can go in or out]. For this process we can show that the enthalpy remains constant.



**INITIAL:** Push piston in and the gas volume goes from  $V_i$  to 0 but the pressure stays constant as the gas escapes through the small porous plug or throttling valve. Thus the work done **on the gas is:** 

$$W_{i} = -p_{i} (0 - V_{i}) = p_{i} V_{i}$$

**FINAL:** The RHS piston is pushed out by the gas at a lower constant pressure and the gas volume goes from 0 to V<sub>f</sub>. Thus the work done **by the gas is:** 

$$W_{f} = -p_{f}(V_{f} - 0) = -p_{f}V_{f}$$

Since the process is adiabatic q = 0 and the first law gives  $\Delta U = w$ . Thus

$$U_f - U_i = w_i + w_f = p_i V_i - p_f V_f$$
$$U_i + p_i V_i = U_f + p_f V_f$$
Thus  $H_i = H_f$  and  $\Delta H = 0$  : process is isenthalpic

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The overall physical result of the gas expansion through the valve is that when the pressure changes from  $p_i$  to  $p_f$  there is a temperature change in the gas from  $T_i$  to  $T_f$ . The temperature and pressure changes are easy to measure and the ratio  $\delta T = (\partial T)$ 

atio  $\frac{\delta T}{\delta p}\Big|_{H} \approx \left(\frac{\partial T}{\partial p}\right)_{H} = \mu_{JT} \text{ is defined as the Joule Thompson coefficient.}}$  $H(T, p) \qquad \qquad For ideal \ gas, H = ft$  $dH = \left(\frac{\partial H}{\partial T}\right)_{p} dT + \left(\frac{\partial H}{\partial p}\right)_{T} dp \qquad \qquad \left(\frac{\partial H}{\partial p}\right) = 0$ for isenthalpic = 0

$$0 = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$
$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{1}{C_p} \left(\frac{\partial H}{\partial p}\right)_T$$
$$\left(\frac{\partial T}{\partial p}\right)_H = \mu_{JT}$$

For ideal gas, H = f(T) only  $\left(\frac{\partial H}{\partial p}\right)_T = 0$ for real gas  $\left(\frac{\partial H}{\partial p}\right)_T \neq 0$ 

In almost all cases the JT coefficient is positive in value. This means that when a gas expands and pressure drops  $\delta p < 0$  via a JT process,  $\delta T < 0$  and the gas cools. This is the principle behind the cooling and liquefaction of gases that is used in refrigeration.

### **Properties of the Joule Thompson coefficient**

 $\mu_{JT}$  = fn(T,p) of each gas and so its value changes with temperature and pressure at which the expansion occurs.

 $\mu_{JT} > 0$  for most T and p conditions but under certain conditions it can be negative. Then the gas will heat up instead of cooling when the expansion occurs. The temperature at which  $\mu_{JT} =$ 0 is called the **inversion temperature**.

•The inversion temperatures for three real gases, nitrogen, hydrogen, and helium.



#### **Gas Liquefaction:**

The diagram shows how a gas can be liquefied by repeated circulation of a gas undergoing JT cooling.

First, the gas is compressed. This heats up the gas but it is cooled down partially through a heat exchanger (cooling vanes) to the ambient temperature.

The gas passes expands through a valve and undergoes JT cooling. It is then made to re-circulate and cool the incoming gas.



Repeating this cycle eventually gets the temperature of the gas exiting the valve below the boiling point and the gas condenses. This was the method used to first liquefy nitrogen and oxygen gas. Hydrogen and helium have low inversion temperatures and thus must be pre-cooled before undergoing JT cooling.

### **Refrigeration:**

Principle of Operation: The freon is compressed by the motor (bottom, back of the fridge). This heats the freon but it is cooled back to near ambient temperature by the heat exchanger (metal grid at back of fridge which feel warm). The compressed freon enters the expansion coils in the freezer compartment where it cools down. Then it undergoes JT expansion and condenses. The fan circulates the air between the main compartment and the freezer. The warmer air from the main compartment provides the heat of vaporization used to evaporate the freon which returns as a gas to the compressor. Thus the fridge air cools. This is the cold air which re-circulates to cool the freezer and the main compartment.



For freon  $\mu_{JT} = 1.2$  K atm<sup>-1</sup>. Thus for a pressure drop of 40 atm in the fridge the temperature drop of the freon is  $\delta T = \mu_{JT} \delta p$ = -48 K which is more than enough to get the freezer compartment to about -15 °C required to keep ice cream quite solid.

### **Carnot Heat engine**

Heat engine is defined as a device that converts heat energy into mechanical energy **through a cyclic process OR** more exactly a **system** which operates continuously and only **heat** and **work** may pass across its boundaries.



HTER= High Temperature Energy Reservoir LTER= Low Temperature Energy Reservoir

The engine consists of an idealized cylinder with a piston that can slide without friction and can do work on the surroundings or have the surrounding do work on the gas.

### You wants to see the engine:

http://galileoandeinstein.physics.virginia.edu/more\_stuff/flashlets/carnot.htm<sub>8</sub>

### **Description of the Carnot Cycle:** The cycle is performed through a sequence of four stages that

system return to its initial state at the end.

### Stage 1: Reversible isothermal expansion from A to B

In the first stage, the piston moves downward while the engine absorbs heat from a source and gas begins to expand. **Isothermal expansion**, because the temperature of the gas does not change.

### Stage 2: Reversible adiabatic expansion from B to C

In the second stage, the heat source is removed; the piston continues to move downward and the gas is still expanding while cooling (lowering in temperature). **Adiabatic expansion** because energy stays.

### Stage 3: Reversible isothermal compression from C to D

The piston begins to move upward (the surrounding do work on the system), which evolve heat  $q_2$  and which goes to sink. The engine gives energy to the environment.

### Stage 4: Reversible adiabatic compression from D to A

In the final stage, the piston to move upward and the cool gas is isolated and compressed. Its temperature rises to its original state. Point C to point D illustrate this behavior; a continuing increase in pressure and decrease in volume to their initial position. Energy stays, so it's an adiabatic compression.  $\int_{a}^{p} \int_{a}^{A} \Delta U_{1} = q_{1} + W_{1}$ 







Programmed by Wan Ching Hui



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The change in U of the system for the cycle  $\Delta U_{cy}$  is:

$$\Delta U_{cy} = \Delta U_1 + \Delta U_2 + \Delta U_3 + \Delta U_4 = zero$$
  
$$\Delta U_{cy} = 0 = (q_1 + q_2) + (W_1 + W_2 + W_3 + W_4)$$
  
$$\Delta U_{cy} = 0 = q_{cy} + W_{cy}$$
  
$$-W_{cy} = q_{cy} = (q_1 + q_2)$$

For Carnot heat engine, it is consider that:

$$\therefore |W_{cy}| = |q_1| - |q_2|$$

Thus, the work  $|W_{cy}|$  done by the engine in a cycle is equal to the difference between the heat in  $|q_1|$  and the heat  $out|q_2|$ .

In practice, the low-temperature reservoir of a heat engine is often the atmosphere so that the economic cost of producing work in the surroundings is mainly that of supplying  $q_1$ .

### Efficiency ε of a heat engine:

It is the ratio of the work done on the surrounding to the heat input at the higher temperature.

$$\varepsilon = \frac{-W_{cy}}{q_1} = \frac{|W_{cy}|}{q_1} = 1 - \frac{|q_2|}{|q_1|}$$
$$0 < \varepsilon < 1$$

It is clear that to increase the value of  $\boldsymbol{\varepsilon}$  of a Carnot heat engine, one would like to reduce heat rejected to the cold reservoir  $q_2$ , which is impossible to be zero.

# **Application in engines**

The Carnot Cycle forms the perfect process of a heat engine. Many engineers tried to reach this kind of cycle. Rudolf Diesel had the most success and his engine is nearly as perfect as the Carnot engine. There are also other cycles, e.g. the Stirling Cycle you see on the right side.



**Description of the Carnot Cycle:** The cycle is performed through a sequence of four stages that system return to its initial state at the end.

*Stage 1:* Reversible isothermal expansion from  $V_1$  to  $V_2$  at  $T_1$ 

$$W_{1} = -nRT_{1} ln\left(\frac{V_{2}}{V_{1}}\right)$$

Stage 2: Reversible adiabatic expansion from  $V_2T_1$  to  $V_3T_2$ 

$$W_2 = \int_{T_1}^{T_2} C_V dT$$

Stage 3: Reversible isothermal compression from  $V_3$  to  $V_4$  at  $T_2$ 

$$W_{3} = -nRT_{2} ln\left(\frac{V_{4}}{V_{3}}\right)$$

Stage 4: Reversible adiabatic compression from  $V_4T_2$  to  $V_1T_1$ 

$$W_4 = \int_{T_2}^{T_1} C_V dT$$

 $\int_{a}^{p} \int_{a}^{A} \Delta U_{1} = q_{1} + W_{1}$ 



$$P t U_3 = q_2 + W_3$$



$$\therefore W_{cy} = W_{1} + W_{2} + W_{3} + W_{4}$$

$$W_{cy} = -nRT_{1} ln\left(\frac{V_{2}}{V_{1}}\right) + \int_{T_{1}}^{T_{2}} C_{V} dT - nRT_{1} ln\left(\frac{V_{3}}{V_{4}}\right) + \int_{T_{2}}^{T_{1}} C_{V} dT$$

$$W_{cy} = -nRT_{1} ln\left(\frac{V_{2}}{V_{1}}\right) - nRT_{2} ln\left(\frac{V_{4}}{V_{3}}\right)$$

$$W_{cy} = -nRT_{1} ln\left(\frac{V_{2}}{V_{1}}\right) + nRT_{2} ln\left(\frac{V_{3}}{V_{4}}\right)$$

*From the* adiabatic process: from  $V_2$  to  $V_3$  and from  $T_1$  to  $T_2$ 

$$\begin{pmatrix} \frac{T_2}{T_1} \end{pmatrix} = \begin{pmatrix} \frac{V_2}{V_3} \end{pmatrix}^{\alpha - l} \quad \alpha = \begin{pmatrix} \frac{C_p}{C_v} \end{pmatrix} \quad \therefore T_1 (V_2)^{\alpha - l} = T_2 (V_1)^{\alpha - l}$$
$$\begin{pmatrix} \frac{T_1}{T_2} \end{pmatrix} = \begin{pmatrix} \frac{V_4}{V_1} \end{pmatrix}^{\alpha - l} \quad \therefore T_1 (V_1)^{\alpha - l} = T_2 (V_4)^{\alpha - l}$$
$$\therefore \begin{pmatrix} \frac{V_2}{V_1} \end{pmatrix} = \begin{pmatrix} \frac{V_3}{V_4} \end{pmatrix}$$

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$$\therefore \left(\frac{V_2}{V_1}\right) = \left(\frac{V_3}{V_4}\right)$$

Substitute in W<sub>cy</sub> equation

$$W_{cy} = -nR(T_1 - T_2) ln \left(\frac{V_2}{V_1}\right)$$
$$q_1 = -W_{cy} = nRT_1 ln \left(\frac{V_2}{V_1}\right)$$

and

Substitute in in the efficiency equation

$$\mathcal{E} = \frac{W_{cy}}{q_1} = \frac{T_1 - T_2}{T_1} = 1 - \left(\frac{T_2}{T_1}\right)$$

Thus, high efficiencies are obtained if the ratio  $T_2/T_1$  is small.

In practice,  $T_2$  is close to room temperature and  $T_1$  is made as high as possible.

## Second Law of thermodynamics

Kelvin's statement "It is impossible to produce work in the surrounding using a cyclic process connected to a single heat engine reservoir"

Clausius' statement "It is impossible to carry out a cyclic process using an engine connected to two heat reservoirs that will have as its only effect the transfer of a quantity of heat from the low-temperature reservoir to the high-temperature reservoir"

$$\mathcal{E} = \frac{W_{cy}}{q_1} = \frac{T_1 - T_2}{T_1} = I - \left(\frac{T_2}{T_1}\right) \quad \text{For any fluid}$$

Types of possible processes:

### (a) SPONTANEOUS(irreversible):

these occur naturally without any effort on our part: mixing of two gases heat flow from a hot to cold body forgetting the second law spending money today becomes tomorrow things never are as they were

### (b) UNNATURAL:

these only occur with energy or work input on our part separating gases in a mixture:

heat flow from a cold to hot body

learning the second law

earning money

### (c) EQUILIBRIUM(reversible):

these show no overall change and are easily reversed balanced budget

knowledge of thermodynamics two minutes after the final exame evaporation « condensation of water in a closed bottle.

# Second Law of Thermodynamics

- It is very important law in chemistry, because it tell us whether a reaction will occur or not and in which direction.
- A new state function (entropy) will appear, which will tell us whether a chemical reaction or physical process can occur spontaneously or not.

# ENTROPY



Matter tends to become disordered



Energy tends to become disordered

## Entropy

From the efficiency of a reversible Carnot engine

$$\mathcal{E} = 1 + \frac{q_2}{q_1} = 1 - \left(\frac{T_2}{T_1}\right) \qquad \therefore \frac{q_2}{q_1} + \frac{T_2}{T_1} = 0$$
$$X\left(\frac{q_1}{T_2}\right) \qquad \therefore \frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$$

where

$$dS = \frac{dq}{T}$$

This is the change in entropy and it is a state function.

The change in a state function around any cycle is zero

$$\therefore \Delta S_{cy} = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$$

: 
$$\Delta S_{cy} = \frac{q_1}{T_1} + 0 + \frac{q_2}{T_2} + 0$$

Where for adiabatic steps:

$$\Delta S_2 = \Delta S_4 = zero$$

Because there is no change in entropy

$$\oint \frac{dq_{rev}}{T} = 0$$
  
$$\therefore \oint dS = 0$$

## Chemical thermodynamics Second Law

•The thermodynamic temperature scale is defined so that during a *reversible* cycle among states that returns to the original state, the integral of dq/T is zero. Hence there exists another variable of state *S*, the entropy, whose change is given by:

$$dS = \frac{dq}{T}$$

•If at any time our closed cycle deviates from reversibility and undergoes a spontaneous change, we find that the integral of dq/T is always positive.

## The Clausius Theorem

According to Carnot theory "No engine operating between two heat reservoirs can be more efficient than a reversible Carnot engine operating between the same two reservoirs"



Where  $q_2$  and  $q_{2(rev)}$  have negative sign

$$\therefore \frac{-q_2}{q_1} \ge \frac{T_2}{T_1} \qquad \text{OR} \quad \therefore \frac{-q_2}{T_2} \ge \frac{q_1}{T_1} \qquad \text{OR} \quad 0 \ge \frac{q_2}{T_2} + \frac{q_1}{T_1}$$

This equation were derived before in the case of reversible Carnot engine, and for the four steps of the cycle:

$$\sum \frac{q_i}{T_i} \le 0$$
<sup>27</sup>

This apply for any engine operating in a cyclic with many heat reservoirs. As in general:

$$\oint \frac{dq}{T} \le 0$$

#### It concluded that:

- If any part of the cyclic process is irreversible (natural), the inequality (<) applies and the cyclic integral is negative.
- If a cyclic process is reversible, the equality applies exactly as Carnot cycle.
- It is impossible for the cyclic integral to be greater than zero.

Note that the temp. that appears in the cyclic integral in the above equation is that of the heat reservoir or surr. When the process is reversible,  $T_{surr} = T_{sys}$ .

The second Law in Practical Applications

By applying the Clausius theorem to an irreversible cycle:

State 1  $\xrightarrow{irreversible}$  State 2  $\xrightarrow{reversible}$  State 1

According to the above equation:

$$\int_{I}^{2} \frac{dq_{irrev}}{T} + \int_{2}^{I} \frac{dq_{rev}}{T} < 0 \qquad \int_{I}^{2} \frac{dq_{irrev}}{T} - \int_{I}^{2} dS < 0$$
  
• Thus  

$$\therefore \Delta S = \int_{I}^{2} dS > \int_{I}^{2} \frac{dq_{irrev}}{T}$$
  
• OR  

$$dS > \int \frac{dq_{irrev}}{T}$$

• This for an infinitesimal irreversible process in an isolated system and represent a second definition of the entropy.

#### The full definition of entropy

By applying the Clausius theorem to an irreversible: cycle:

$$dS \geq \int \frac{dq_{irrev}}{T}$$

This represent the second Law in the useful form.

• The equation describes three types of processes:

$$dS > \frac{dq}{T}$$
 Spontaneous and irreversible process  

$$dS = \frac{dq}{T}$$
 Reversible process  

$$dS < \frac{dq}{T}$$
 Impossible process

#### For closed system dq = zero for finite change

- $\Delta S > 0$  Spontaneous and irreversible process
- $\Delta S = 0$  Reversible process
- $\Delta S < 0$  Impossible process

Changes in entropy of an isolated system with time

S increases spontaneously until equilibrium is reached.

The thermodynamic does not give the time required to reach equilibrium, but it gives the direction.



### **Entropy changes in reversible processes**

#### Relation between entropy change and enthalpy

The transfer of heat from a body to another at infinitesimally change of temperature is reversible.

Example: vaporization of a pure liquid into its vapor at the equilibrium vapor pressure and constant T.  $Liquid(T, p) \longrightarrow Vapor(T, p)$ 

$$\int_{S_{1}}^{S_{2}} ds = \int_{1}^{2} \frac{dq_{rev}}{T} = S_{2} - S_{1} = \Delta S = \frac{q_{rev}}{T}$$

Where  $q_{rev}$  is the heat absorbed in the reversible change at constant p and is equal to  $\Delta H$ .

$$\therefore \Delta S = \frac{\Delta H}{T}$$

This equation can be used to calculate  $\Delta S$  of sublimation, melting, ... etc.

Ex: n-hexane boils at 58.7 °C at 1 atm and its  $\Delta H_{vap,m}$  is 28.85 kJ mol<sup>-1</sup>at this temperature. What is  $\Delta S_{vap}$  of n-hexane when it vaporized at the boiling point?

$$\Delta S_{vap,m} = \frac{\Delta H_{vap,m}}{T} = \frac{28850 J / mole}{(278.1 + 58.7)K} = 84.41 J / (K.mole)$$

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### $\Delta S(liquid) > \Delta S(solid)$ At equilibrium

This means that entropy is a measure of the disorder of the system.

Note: the molecules of gas are more disorder than those of liquid and the molecules of liquid are more disorder than those of solid .



The general equation for change in entropy for reversible processes:

$$\Delta S = S_f - S_i = \int_i^f dS = \int_i^f \frac{dq_{rev}}{T}$$

(a) Adiabatic 
$$dq_{rev} = 0$$

$$\Delta S = \int 0/T = 0$$

b) Isothermal 
$$T = constant$$
  

$$\Delta S = \int_{i}^{f} \frac{dq_{rev}}{T} = \frac{1}{T} \int_{i}^{f} dq_{rev}$$

$$\Delta S = \frac{q_{rev}}{T}$$

(c) Isobaric

p = constant

$$\begin{split} dq_{rev}|_p &= dH|_p = C_p \; dT \\ \Delta S &= \int_{T_i}^{T_f} \frac{C_p dT}{T} = C_p \int_{T_i}^{T_f} \frac{dT}{T} & \text{and} \quad \text{if } C_p \; \text{ is independent of } T \end{split}$$



 $\Delta S = \frac{\Delta H}{\Delta H}$ 

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(d) Isothermal, Isobaric

$$\Delta S = \frac{q_{rev} |_{p}}{T} \qquad q_{rev} |_{p} = \Delta H$$

#### (e) Isochoric V = constant

$$\therefore dw_{rev} = 0 \quad \therefore dU = dq_{rev}I_v = C_v dT$$
$$\Delta S = \int_{T_i}^{T_f} \frac{C_v dT}{T} = C_v \int_{T_i}^{T_f} \frac{dT}{T} \qquad \text{for } C_v \text{ is independent of } T$$

(e) Isothermal and Ideal Gas where 
$$V_i \rightarrow V_f$$
  
For isothermal conditions  $\Delta S = \frac{q_{rev}}{T}$   
For isothermal, ideal gas, reversible conditions

recall 
$$\Delta U = 0$$
  $q_{rev} = -w_{rev} = nRT \ln\left(\frac{V_f}{V_i}\right)$ 

### (g) Ideal Gas: Any Process going from state $T_i,\,p_i,\,V_i \to T_f,\,p_f,\,V_f$

 $dq_{rev} = dU - dw_{rev}$   $dw_{rev} = -p dV$ reversible

 $dU = C_v dT$   $\therefore dq_{rev} = C_v dT + p dV = C_v dT + nRT dV/V$ ideal gas

$$\Delta S = \int \frac{dq_{\rm rev}}{T} = \int \frac{C_v dT + nRTdV/V}{T} = \int_{T_i}^{T_f} \frac{C_v dT}{T} + nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$\Delta S = C_v \ln \left(\frac{T_f}{T_i}\right) + nR \ln \left(\frac{V_f}{V_i}\right)$$

$$\Delta \mathbf{S} = \mathbf{n}\mathbf{R}\ln\left(\frac{\mathbf{V}_{\mathbf{f}}}{\mathbf{V}_{\mathbf{i}}}\right)$$

$$\Delta \mathbf{S} = \mathbf{n} \mathbf{R} \ln \left( \frac{\mathbf{V}_{\mathbf{f}}}{\mathbf{V}_{\mathbf{i}}} \right)$$

 $\Delta S = C_v \ln \left(\frac{T_f}{T_c}\right)$ 

$$\Delta S = C_v \ln \left(\frac{T_f}{T_i}\right) + nR \ln \left(\frac{V_f}{V_i}\right) \qquad \text{id}$$

deal gas, any process

This equation for an ideal gas is extremely useful because it applies to any process and only requires a knowledge of the initial and final state i.e. any two of temperature, pressure and volume. It can be used instead of some of those equations derived earlier since it reduces to those previously derived.

For example, if the process is isobaric then  $p_i = p_f$  and  $\frac{V_i}{T_i} = \frac{V_f}{T_f}$  or  $\frac{V_f}{V_i} = \frac{T_f}{T_i}$ 

Substituting in the above general equation for an ideal gas

$$\Delta S = C_v \quad \ln\left(\frac{T_f}{T_i}\right) + nR \quad \ln\left(\frac{T_f}{T_i}\right) = (C_v + nR) \quad \ln\left(\frac{T_f}{T_i}\right) \quad \longrightarrow \quad \Delta S = C_p \quad \ln\left(\frac{T_f}{T_i}\right)$$

If the process is adiabatic we recall that:

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$$\frac{\mathbf{T}_{\mathbf{f}}}{\mathbf{T}_{\mathbf{i}}} = \left(\frac{\mathbf{V}_{\mathbf{i}}}{\mathbf{V}_{\mathbf{f}}}\right)^{1/c} \quad \text{where} \quad \mathbf{c} = \frac{\mathbf{C}_{\mathbf{v}}}{\mathbf{nR}} \qquad \Delta \mathbf{S} = \mathbf{C}_{\mathbf{v}} \quad \ln\left(\frac{\mathbf{V}_{\mathbf{i}}}{\mathbf{V}_{\mathbf{f}}}\right)^{1/c} + \mathbf{nR} \quad \ln\left(\frac{\mathbf{V}_{\mathbf{f}}}{\mathbf{V}_{\mathbf{i}}}\right) = \frac{\mathbf{C}_{\mathbf{v}}}{c} \ln\left(\frac{\mathbf{V}_{\mathbf{i}}}{\mathbf{V}_{\mathbf{f}}}\right) - \mathbf{nR} \quad \ln\left(\frac{\mathbf{V}_{\mathbf{i}}}{\mathbf{V}_{\mathbf{f}}}\right)$$
$$\mathbf{But} \quad \frac{\mathbf{C}_{\mathbf{v}}}{c} = \mathbf{nR} \quad \therefore \Delta \mathbf{S} = \mathbf{0}$$

### $\Delta S$ for **Irreversible Processes**:

Consider a system going from an initial to a final state by a reversible path and an irreversible path.



### How can we get $\Delta S_{svs}$ for the irreversible path?

Note that  $(q_{sys})_{irrev} \neq (q_{sys})_{rev}$  since Path A and Path B are different. On the other hand entropy is a state function and the final state is the same for both paths and so  $\Delta S_{sys}$  for the two paths must be the same. Thus the way to get  $(\Delta S_{sys})_{irrev}$  is to devise a reversible path from the initial to the final state and use the equations developed for the reversible case.

Find the value of  $\Delta S$  of the system, surroundings and universe when 2 mol of N<sub>2</sub> at 300 K doubles in volume from 4 to 8 L for various processes. Assume that the gas is ideal and that  $Cv,m = 20.8 J K^{-1} mol^{-1}$ .

1. Reversible, isothermal:	Initial State	Final State
	300 K	300 K
	4 L	8 L
	$p_i = nRT_i/V_i$	p <sub>f</sub> =nRT <sub>f</sub> /V <sub>f</sub>
	= 2x.08206x300 L atm/4 atm	-
Analysis:	=12.3 atm	=6.15 atm

*Isothermal expansion so entropy of system should increase* Process is reversible so by the second law

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

 $\Delta S_{univ} = \Delta S_{svs} + \Delta S_{surr}$ Since Since gas is ideal gas we only need to know the initial and final states to find the change in the system entropy via the general equation.

#### **Calculation:**

General equation for ideal gas  $\Delta S = C_v \ln \left(\frac{T_f}{T_i}\right) + nR \ln \left(\frac{V_f}{V_i}\right)$ 

Since  $T_i = T_f$  the equation reduces to  $\Delta S = nR \ln \left(\frac{V_f}{V_i}\right) = 2 \operatorname{mol} x 8.314 \text{ J K}^{-1} \operatorname{mol}^{-1} \ln(8/4)$  $= 11.5 \text{ J K}^{-1}$ 

 $w = -nRT \ln\left(\frac{V_f}{V_i}\right) = -q = -2 \mod x \ 8.314 \ JK^{-1} \mod^{-1} x \ 300 \ T \ln(8/4) = -3450 \ J$ Note:  $\Delta S = q_{rev} / T = 3450 \text{ J}/300 \text{ K} = 11.5 \text{ J/K}$  as before.

# 2. Irreversible, isothermal expansion against constant external pressure of 1 atm (until volume reaches 8 L). The initial and final states are as before.

	Initial	Final
	300 K	300 K
	4 L	8 L
	12.3 atm	6.15 atm
<u>Analysis</u>		
System in same is f	inal state as in 1	$\Delta S_{sys} = 11.5 \ J \ K^{-1}$
As in case 1, heat l	ost by surroundings so	$\Delta S_{surr} = q_{surr}/T < 0$
Process is irreversi	ble so by the Second Law	$\Delta S_{univ} > 0$

#### **Calculation**

To get  $\Delta S_{surr}$  need to get the heat transferred to the system to keep the gas temperature constant when the gas expands. For ideal gas, isothermal process

 $\Delta U_{sys} = 0$  and  $q_{sys} = -w_{sys}$ 

For constant external pressure  $-w = p_{ext} \Delta V = 1 \text{ atm } (8-4)L = 4 L \text{ atm.}$ 

Also  $q_{surr} = -q_{sys} = -4 L \text{ atm} = -404 \text{ J}$  Thus  $\Delta S_{surr} = -404 \text{ J}/300 \text{ K} = -1.35 \text{ J} \text{ K}^{-1}$ 

Thus  $\Delta S_{univ} = 11.5 - 1.35 = 10.2 \text{ J K}^{-1}$ .

#### 3. Reversible, Adiabatic Expansion to final volume of 8 L

Initial stateFinal state300 K $T_f$  gas must cool4 L8 L12.3 atm $p_f$  pressure drops for expansion

Analysis:

 $T_f$  - adiabatic expansion so gas must cool

ideal gas, reversible, adiabatic

$$T_f < 300 \ K$$
$$T_f = \left(\frac{V_i}{V_f}\right)^{1/c} T_i$$

 $p_f$  - gas expands and also cools so pressure must decrease  $p_f < 12.3$  atm

ideal gas equation 
$$p_f = \frac{nRT_f}{V_f}$$

 $\Delta S_{sys}$  - reversible, adiabatic-  $dq_{rev} = 0$ ;  $\Delta S_{sys} = \int \frac{dq_{rev}}{T} \Delta S_{sys} = 0$ 

It may seem odd that  $\Delta S_{sys} = 0$  because entropy increases when gas expands but this is offset by the entropy decrease due to the cooling.

$$\Delta S_{univ}$$
 - since process is reversible, by the Second Law  $\Delta S_{univ} = 0$ 

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

#### **Calculation:**

All entropy changes already calculated by simple analysis but we should calculate T<sub>f</sub> and p<sub>f</sub>.

$$T_{f} = \left(\frac{V_{i}}{V_{f}}\right)^{1/c} T_{i} \qquad c = \frac{C_{v,m}}{R} = \frac{20.81}{8.314} = 2.5 \qquad T_{f} = 300 \quad K \quad \left(\frac{4}{8}\right)^{1/2.5} = 227 \quad K$$

Having found the final T and knowing the final volume the ideal gas law is used to find p<sub>f</sub>,

$$p_{f} = \frac{nRT_{f}}{V_{f}} = \frac{2 \text{ mol } x .08206 \text{ L atm } \text{K}^{-1} \text{ mol}^{-1} \text{ x } 227 \text{ K}}{8 \text{ L}} = 4.66 \text{ atm}$$

For interest the work and energy are calculated:

 $w = \Delta U = nC_{v,m} \Delta T = 2 \mod x \ 20.8 \ J \ K^{-1} \mod^{-1} (227 - 300) \ K = -3037 \ J$ Comment: the value is negative since work is done by the gas and the gas cools.

#### 4. Irreversible Adiabatic Expansion to 8 L against a constant external pressure of 1 atm.

	Initial State Final St		ate
	300 K	$T_{f}$	
	4 L	8 L	
	12.3 atm	pf	
<u>Analysis</u> :		-	
$T_f$ - adiabatic ex	pansion so gas cools	5	T <sub>f</sub> < 300 K
But coolin	g is not as great as i	n reversible case	$T_{f} > 227 \text{ K}$
Equation	$T_{f} = T_{i} - \frac{p_{ext}\Delta}{C_{V}}$	V	
<b>p</b> <sub>f</sub> - gas expands	and also cools so pr	essure must decrease	p <sub>f</sub> < 12.3 atm
But decrease	is not as large as in	reversible case since	
T <sub>f</sub> is higher	and V <sub>f</sub> the same		p₁ >4.66 atm
Use ideal gas	equation		

$$\Delta S_{univ}$$
 - process is irreversible so  $\Delta S_{univ} > 0$ 

 $\Delta S_{surr}$  - process is adiabatic so  $q_{surr} = -q_{sys} = 0$   $\Delta S_{surr} = 0$ 

$$\Delta S_{sys}$$
 - Since  $\Delta S_{surr} = 0$  then  $\Delta S_{sys} = \Delta S_{univ}$   $\Delta S_{sys} > 0$ 

Need to devise reversible path to get  $dq_{rev}$ , then integrate  $\Delta S_{sys} = \int \frac{dq_{rev}}{T}$ 

But, since gas is ideal we can use the general equation.

$$\Delta \mathbf{S} = \mathbf{C}_{\mathbf{v}} \ln \left( \frac{\mathbf{T}_{\mathbf{f}}}{\mathbf{T}_{\mathbf{i}}} \right) + \mathbf{n} \mathbf{R} \ln \left( \frac{\mathbf{V}_{\mathbf{f}}}{\mathbf{V}_{\mathbf{i}}} \right)$$

Calculation

$$T_{f} \qquad T_{f} = T_{i} - \frac{p_{ext}\Delta V}{C_{V}} = 300 \quad K - \frac{1 \quad atm \quad (8-4)Lx \ 101 J/Latm}{2 \quad mol \quad x \quad 20.8 \quad J \quad K^{-1} \quad mol^{-1}}$$

$$= 300 - 9.7 = 290.3$$
 K

 $p_f = nRT_f / V_f = 2 x .08206 x 290.3 / 8 = 5.96 atm$ 

$$\Delta S_{sys} = nR \ln \frac{V_f}{V_i} + nC_{v,m} \ln \frac{T_f}{T_i} = 2 \times 8.314 \text{ J } \text{K}^{-1} \ln \frac{8}{4} + 2 \times 20.8 \text{ J } \text{K}^{-1} \ln \frac{290.3}{300}$$
  
$$\Delta S_{sys} = 11.5 - 1.4 = 11.1 \text{ J } \text{K}^{-1} = \Delta S_{univ}$$

#### SUMMARY OF EXAMPLE

	isothermal	isothermal	adiabatic	adiabatic
	reversible	irreversible	reversible	irreversible
		against 1 atm		against 1 atm
$\Delta S_{sys}$ J K <sup>-1</sup>	11.5	11.5	0	10.1
$\Delta S_{surr}$ J K <sup>-1</sup>	-11.5	-1.35	0	0
$\Delta S_{univ}$ J K <sup>-1</sup>	0	10.2	0	10.1
T <sub>f</sub> K	300	300	227	290
V <sub>f</sub> L	8	8	8	8
p <sub>f</sub> atm	6.15	6.15	4.66	5.96
q	3450	404	0	0
w J	-3450	-404	-3037	-404
$\Delta U$	0	0	-3037	-404

### **ABSOLUTE ENTROPIES AND THE THIRD LAW**

The experimental observation showed that changes in entropy approach zero as the temperature approaches zero.

### The statement:

### The entropy of a perfect crystal is zero at 0 K

This is because a perfect crystal one in which all the atoms are perfectly ordered in their lattice positions.

### The equation:

$$\Delta \mathbf{S} = \mathbf{S}(\mathbf{T}) - \mathbf{S}(\mathbf{0}) = \int_{0}^{T} \frac{d\mathbf{q}_{rev}}{T} = \int_{0}^{T} \frac{\mathbf{C}_{p} d\mathbf{T}}{T} \qquad \text{where } \mathbf{S}(\mathbf{0}) = \mathbf{0}$$

In going from 0 K to some temperature T we need to account for the possibility that the compound passes through all its physical states of solid, liquid and gas. At each temperature where a phase transition occurs there will be an entropy jump given by  $\Delta S = \frac{\Delta H_{phase transition}}{T_{transition}}$ 

#### Thus the most general change in the compound is

$$solid(0 \text{ K}) \rightarrow solid(T_m) \rightarrow liquid(T_m) \rightarrow liquid(T_b) \rightarrow gas(T_b) \rightarrow gas(T)$$

$$\mathbf{S}(\mathbf{T}) == \int_{0}^{T_{m}} \frac{\mathbf{C}_{p}(\mathbf{s})d\mathbf{T}}{\mathbf{T}} + \frac{\Delta_{fus}\mathbf{H}}{T_{m}} + \int_{T_{m}}^{T_{b}} \frac{\mathbf{C}_{p}(\mathbf{l})d\mathbf{T}}{\mathbf{T}} + \frac{\Delta_{vap}\mathbf{H}}{T_{b}} + \int_{T_{b}}^{T} \frac{\mathbf{C}_{p}(\mathbf{g})d\mathbf{T}}{\mathbf{T}}$$

$$\mathbf{S} = \begin{bmatrix} \frac{\Delta_{vap}\mathbf{H}}{T_{b}} \\ \frac{\Delta_{tas}\mathbf{H}}{T_{m}} \end{bmatrix}$$

$$\mathbf{T}_{m} = \mathbf{T}_{b}$$

# There are two types of randomness in crystals at absolute zero are ignored in calculating entropies for chemical purpose only:

- Most crystals are made up of a mixture of isotopes species. Because the reactants and products I a rxn contain the same mixture of isotopes, their entropies are ignored.
- 2. There is a nuclear spin at 0K that is ignored because it exists in both reactants and products.

### **Entropy Change s for chemical reactions:**

$$\Delta_{\rm r} S^{\theta} = \sum_{\rm products} \nu S^{\theta} - \sum_{\rm reactants} \nu S^{\theta}$$

Recall that  $\theta$  stands for the standard pressure of 1 atm (or 1 barr). As before the temperature is taken as 298 K and S<sup> $\theta$ </sup>(298) values are given in Tables of thermodynamic data.

#### Example: Fermentation of sugar [ $\alpha$ -D glucose] to give alcohol

$$C_6 H_{12} O_6(aq) \rightarrow 2 C_2 H_5 OH(l) + 2 CO_2 (g)$$

 $S^{\theta} J K^{-1} mol^{-1}$  264 161 213.6  $\Delta_r S^{\theta} = \sum_{\text{products}} v S^{\theta} - \sum_{\text{reactants}} v S^{\theta}$  $\Delta S^{\theta} = 2(161) + 2(213.6) - 264 = 485.2 \text{ J K}^{-1} mol^{-1}$ 

Value is > 0 since there are more products than reactants and especially because of the gaseous product

### How to calculate $S^{\theta}$ values at any temperature?

$$S^{\theta}(T) = S^{\theta}(298) + \int_{298}^{T} \frac{C_p dT}{T} + \text{ any phase change terms}$$

Example: Calculate S<sup> $\theta$ </sup>m for silver at 500 K given that Cp,m = 3R and available S<sup> $\theta$ </sup>(298) = 42.68 J K<sup>-1</sup> mol<sup>-1</sup>

.....

$$S_{m}^{\theta}(500) = S_{m}^{\theta}(298) + \int_{298}^{500} \frac{C_{p}(s)dT}{T} = 44.68 + C_{p,m}(s) \ln \frac{500}{298}$$
  
= 42.68 J K<sup>-1</sup> mol<sup>-1</sup> + 3 x 8.314 J K<sup>-1</sup> mol<sup>-1</sup> ln 1.677 = 42.68 + 12.89  
= 55.57 J K<sup>-1</sup> mol<sup>-1</sup>