Thermodynamics 1

- Thermodynamics is the study of <u>thermal processes</u> in <u>macroscopic</u> systems.
- It is usually assumed that a classical thermodynamic system is a *continuum*, with properties that vary smoothly from point to point.
- The number of molecules in a macroscopic system is typically of the order $N_A = 6.02 \times 10^{26} (Avogadro's number)$.
- At STP (0°C and 1 atm), 1 kmole of a gas occupies 22.4 m³.
- The molecular density at STP is 6.02 x 10²⁶/22.4
 ≈ 2.7 x10²⁵ molecules/m³ (*Loschmidt's number*).
- Thus, a cube of side 1 mm contains about 10¹⁶ molecules, while a cube of side 10 nm contains about 10 molecules.
- Clearly, the continuum model breaks down in the latter case₁

Thermodynamics 2

- The central concept of thermodynamics is *temperature*, which cannot be expressed in terms of the fundamental quantities of mass, length and time.
- Temperature is a statistical parameter, which may be defined precisely only for a macroscopic system.
- In this course, we study *equilibrium thermodynamics* from the standpoints of both *classical thermodynamics* and *statistical thermodynamics*.
- Given time, the alternative approach of *Information Theory* will be introduced.
- We ignore the more difficult topic of *non-equilibrium thermodynamics*, except for a brief foray into *kinetic theory*.

Einstein on Thermodynamics

- "A theory is the more impressive the greater the simplicity of its premises, and the more extended its area of applicability.
- Classical thermodynamics... is the only physical theory of universal content which I am convinced that, within the applicability of its basic concepts, will never be overthrown."

Eddington on Thermodynamics

- "If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations – then so much the worse for Maxwell's equations.
- But if your theory is found to be against the second law of thermodynamics I can offer you no hope; there is nothing for it but to collapse in deepest humiliation."

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Thermodynamics 3

- Classical thermodynamics, which was developed in the first half of the nineteenth century by Carnot, Clausius, Joule, Kelvin, and Mayer (and others), is a *phenomenological* theory, dealing with macroscopic phenomena, and avoiding atomic concepts.
- <u>Its strength</u> lies in the generality of its predictions, which are based on the small number postulates set out in the laws of thermodynamics, and apply to all macroscopic systems; e.g. solids, fluids and electromagnetic radiation.
- <u>Its weakness</u> also lies in great generality, since it cannot be applied to real systems without auxiliary input, either experimental or theoretical.
- In particular, the equation of state of a fluid, linking pressure, volume and temperature, must be derived from experiment.⁵

The Laws of Thermodynamics: Summary

Zeroth Law

The temperature θ is introduced via the concept of *thermal* equilibrium.

<u>First Law</u>

Energy conservation in a closed system is used to define both the *heat* Q transferred and the change of *internal energy* of the system ΔU .

<u>Second Law</u>

The *entropy* S of an isolated system is defined as a property of the system which has a maximum at equilibrium; i.e.

$$\Delta S \ge 0$$
, or $S \rightarrow S_{max}$.

<u>Third Law</u>

The entropy $S \rightarrow 0$ as $T \rightarrow 0$.

Isolated, Closed and Open Systems 1

- A *system* is the portion of the physical world being studied.
- The system plus surroundings comprise a *universe*.
- The boundary between a system and its surroundings is the *system wall*.
- If heat cannot pass through the system wall, it is termed an adiabatic wall, and the system is said to be thermally isolated or thermally insulated.
- If heat can pass through the wall, it is termed a *diathermal wall*.
- Two systems connected by a diathermal wall are said to be in thermal contact.

Isolated, Closed and Open Systems 2

- An *isolated system* cannot exchange mass or energy with its surroundings.
- The wall of an isolated system <u>must</u> be adiabatic.
- A *closed system* can exchange energy, but not mass, with its surroundings.
- The energy exchange may be mechanical (associated with a volume change) or thermal (associated with heat transfer through a diathermal wall).
- An **open system** can exchange both mass and energy with its surroundings.

Isolated, Closed and Open Systems 3



Isolated System Neither energy nor mass can be exchanged.

Closed System

Energy, but not mass can be exchanged. Open System Both energy and mass can be exchanged. ⁹

Thermal Equilibrium and the Zeroth Law

- If warm and cool objects are placed in thermal contact, energy, known as *heat*, flows from the warm to the cold object until *thermal equilibrium* is established.
- Zeroth Law of Thermodynamics

Two systems, separately in thermal equilibrium with a third system, are in thermal equilibrium with each other.

- The property which the three systems have in common is known as *temperature* θ.
- Thus the zeroth law may be expressed as follows: if $\theta_1 = \theta_2$ and $\theta_1 = \theta_3$, then $\theta_2 = \theta_3$.

Thermodynamic Variables

- **Thermodynamic variables** are the observable macroscopic variables of a system, such as P, V and T.
- If the are used to describe an equilibrium state of the system, they are known as *state variables*.
- *Extensive variables* depend on the size of the system; e.g. mass, volume, entropy, magnetic moment.
- Intensive variables do <u>not</u> depend on size; e.g. pressure, temperature, magnetic field.
- An extensive variable may be changed to an intensive variable, known as a *specific value*, by dividing it by a suitable extensive variable, such as mass, no.of kmoles, or no. of molecules.
- Example: the specific heat is normally (heat capacity)/(mast).

Equilibrium States

- An *equilibrium state* is one in which the properties of the system do not change with time.
- In many cases, an equilibrium state has intensive variables which are uniform throughout the system.
- A non-equilibrium state may contain intensive variables which vary in space and/or time.
- An equation of state is a functional relationship between the state variables; e.g. if P,V and T are the state variables, then the equation of state has the form f(P, V, T) =0.
- In 3-dimensional P-V-T space,

an equilibrium state is represented by a point, and the equation of state is represented by a surface.

Processes 1

- A *process* refers to the change of a system from one equilibrium state to another.
- The initial and final states of a process are its *end-points*.
- A *quasistatic process* is one that takes place so slowly that the system may be considered as passing through a succession of equilibrium states.
- A quasistatic process may be represented by a *path* (or line) on the equation-of-state surface.
- If it is *non-quasistatic*, only the end-points can be shown.
- A *reversible process* is one the direction can be reversed by an infinitessimal change of variable.
- A reversible process is a quasistatic process in which no dissipative forces, such as friction, are present.
- A <u>reversible change must be quasistatic</u>, but a quasistatic ₁₃ process need not be reversible; e.g. if there is hysteresis.

Processes 2

- An *isobaric* process is one in which the pressure is constant.
- An *isochoric* process is one in which the <u>volume</u> is constant.
- An *isothermal* process is one in which the <u>temperature</u> is constant.
- An *adiabatic* process is one in which no heat enters or leaves the system; i.e. Q = 0.
- An *isentropic* process is one in which the <u>entropy</u> is constant.
- It is a reversible adiabatic process.
- If a system is left to itself after undergoing a non-quasistatic process, it will reach equilibrium after a time t much longer than the <u>longest</u> *relaxation time* т involved; i.e. t » т.
- **Metastable equilibrium** occurs when one particular relaxation time τ_0 is much longer than the time Δt for which the system is observed; i.e. $\tau_0 \gg \Delta t$.

Three Types of Process





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Boyle's Law and the Ideal Gas Scale



- Boyle's Law
- At sufficiently low pressure, the product PV was found to be constant for gases held at a given temperature θ; i.e.

 $PV = f(\theta)$ for $P \rightarrow 0$.

- Fixed points (prior to 1954)
- The ice and steam points were defined to be 0°C and 100°C exactly.
- The ideal gas (or kelvin) scale was defined as

 $T_{\kappa} = T_{c} + 273.15.$

The Ideal Gas Law

- <u>Fixed point</u> (1954)
- The triple point of water is $T_{tr} = 273.16$ K, $P_{tr} = 6.0 \times 10^{-3}$ atm.
- <u>Ideal gas law</u> PV = nRT or Pv = RT,
- where n is the no. of kmoles, v is the volume per kmole, T is the absolute temperature in K, and the gas constant R = 8.314 x 10³ J/(K.kmol).
- For a constant quantity of gas, $P_1V_1/T_1 = P_2V_2/T_2$.



Van der Waals' Equation 1

• The Van der Waals equation of state

 $(P + a/v^2)(v - b) = RT,$

reproduces the behavior of a real gas more accurately than the ideal gas equation through the empirical parameters a and b, which represent the following phenomena.

- i. The term a/v² represents the attractive intermolecular forces, which reduce the pressure at the walls compared to that within the body of the gas.
- ii. The term b represents the volume occupied by a kilomole of the gas, which is unavailable to other molecules.
- As a and b become smaller, or as T becomes larger, the equation approaches ideal gas equation Pv = RT.
- An inflection point, which occurs on the curve at the critical temperature T_c, gives the critical point (T_c, P_c).

Van der Waals' Equation 2



- Below the critical temperature T_c , the curves show maxima and minima. A physically reasonable result is obtained by replacing the portion xy, with a straight line chosen so that $A_1 = A_2$. C is the *critical point*.
- A vapor, which occurs below the critical temperature, differs from a gas₁ in that it may be liquefied by applying pressure at constant temperature.

Thermodynamic Work 1

• <u>Sign convention</u>

The work done by the system is defined to be positive.

With this definition, the work done on the system – the *external work* of mechanics – is negative.

The work done in a <u>reversible</u> process – the **configuration work** – is given by the product of an intensive variable and its complementary external variable; e.g. dW = PdV.

- <u>Reversible isochoric process</u> W = 0, since $\Delta V = 0$.
- <u>Reversible isobaric process</u> $W = P \Delta V = P(V_2 V_1).$
- These results hold for <u>all</u> materials.
- The work done is always positive for expansion and negative for compression.

Thermodynamic Work 2



- Calculating the work done in a reversible isothermal process requires the equation of state of the system to be known.
- <u>Reversible isothermal process for an ideal gas</u> (PV = nRT) $W = \int PdV = nRT \int dV/V = nRT \ln(V_2/V_1).$

In both cases, the work done by the system equals the shaded area under curve.

Thermodynamic Work 3



Reversible cyclic process

 $W = \oint PdV$ equals the area enclosed by the PV curve.

W is <u>positive</u> if the area is traversed in a <u>clockwise</u> sense (as shown), and <u>negative</u> if traversed <u>counter-clockwise</u>.

The equality $W = \int PdV$ applies to reversible processes only. The work done in an irreversible process is given by the inequality $W < \int PdV$.

Expansivity and Compressibility

- An equation of state may be written as
 P = P(V,T), V = V(T,P) or T = T(P,V).
- Thus, for example,

 $dV = (\partial V / \partial T)_P dT + (\partial V / \partial P)_T dP.$

- In general $(\partial x/\partial y)_z (\partial y/\partial z)_x (\partial z/\partial x)_y = -1$, or $(\partial y/\partial x)_z = -(\partial y/\partial z)_x (\partial z/\partial x)_y$.
- Two experimental quantities which may be used to find the equation of state are the following:
 coefficient of volume expansion β ≡ (1/V) (∂V/∂T)_P;
 isothermal compressibility κ ≡ − (1/V) (∂V/∂P)_T.
- Thus $dV = \beta V dT \kappa V dP$.

Useful Theorem

If
$$z = z(x, y)$$
, then
 $dz = \left(\frac{\partial z}{\partial x}\right)_{y} dx + \left(\frac{\partial z}{\partial y}\right)_{x} dy$.
For a process at constant z ,
 $0 = \left(\frac{\partial z}{\partial x}\right)_{y} + \left(\frac{\partial z}{\partial y}\right)_{x} \left(\frac{\partial y}{\partial z}\right)_{z}$.
Thus, $\left(\frac{\partial z}{\partial x}\right)_{y} = -\left(\frac{\partial z}{\partial y}\right)_{x} \left(\frac{\partial y}{\partial z}\right)_{z}$.
Remember the negative signs.
 $ar \qquad \left(\frac{\partial z}{\partial x}\right)_{y} \left(\frac{\partial x}{\partial y}\right)_{z} \left(\frac{\partial y}{\partial z}\right)_{x} = -\frac{41}{1}$.
Example : $\left(\frac{\partial P}{\partial T}\right)_{v} = -\left(\frac{\partial P}{\partial V}\right)_{T} \left(\frac{\partial V}{\partial T}\right)_{p} = \frac{\beta}{\pi} \pi_{T}$,
since $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_{p}$ and $\chi_{T} = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{T}$. 24

Hysteresis

- Hysteresis curves are examples of processes which may be quasistatic, but are <u>not</u> reversible.
- Hysteresis is caused by *internal friction*, and is a well-known feature of *ferromagnetism* and *first-order phase transitions*.
- The specification of the state of a homogeneous system by a small number of thermodynamic variables breaks down in the presence of hysteresis, since the equilibrium state depends on the previous history of the system.



First Law of Thermodynamics



 $\Delta U = Q - W,$

where ΔU is the increase of internal energy of the system, Q is the heat entering the system, and W is the work done by the system.

Microscopic picture

- The internal energy U is made up of the translational and rotational KE, and intermolecular PE of the gas molecules of the system.
- For an *ideal monatomic gas*, U is the total translational KE, known as the *thermal energy*, since it is proportional to T.



 ΔU depends on -W because gas molecules lower speed, thus reducing the KE of the gas.

Exact and Inexact Differentials

• The differential form of the 1st Law is

dU = dQ - dW,

where dU is an *exact differential*, because U is a state variable, and both dQ and dW are *inexact differentials*, since Q and W are not state variables.

• Exact differential dF(x,y)

dF is an exact differential if F(x,y) is a function of the variables x and y. Thus

dF = A(x,y) dx + B(x,y) dy,

where $A(x,y) = (\partial F/\partial x)_y$ and $B(x,y) = (\partial F/\partial y)_x$.

• Inexact differential dF'(x,y)

If dF' = A'(x,y) dx + B'(x,y) dy is an inexact differential, there is no function F'(x,y) from which dF' can be derived.

Tests for an Exact Differential

1. The simplest way of finding if dF(x,y) is an exact differential is to see if $(\partial A/\partial y)_x = (\partial B/\partial x)_y$, since $\partial^2 F/\partial x \partial y = \partial^2 F/\partial y \partial x$, if F = F(x,y).

2. If
$$F = F(x,y)$$
,
then $dF = F(x_2,y_2) - F(x_1,y_1) = F_2 - F_1 = \int_1^2 dF$.
Thus, $\int_1^2 (Adx + Bdy)$ does not depend on path.

3. To find F from dF, use $\int dF = \int A dx + f(y) = \int B dy + g(x)$.

• Note: for a state function F = F(V,T,N), $dF = (\partial F/\partial V)_{T,N} dV + (\partial F/\partial T)_{N,V} dT + (\partial F/\partial N)_{V,T} dN$, and $\partial^2 F/\partial V \partial T = \partial^2 F/\partial T \partial V$, etc.

Heat Capacities

• The heat capacity at constant parameter i is given by

 $C_i = (dQ/dT)_i$.

Note that one cannot use the partial form $(\partial Q/\partial T)_i$, since dQ is an <u>inexact differential</u>.

Heat capacity at Constant Volume Cv

• dQ = dU + PdV, so that $C_v = (dQ/dT)_v = (\partial U/\partial T)_v$.

Heat capacity at Constant Pressure CP

- $C_P = (dQ/dT)_P = (\partial U/\partial T)_P + P(\partial V/\partial T)_P$.
- The enthalpy H is defined as H = U + PV, so that $(dH/dT)_P = (\partial U/\partial T)_P + P(\partial V/\partial T)_P$.

Thus, $C_P = (\partial H / \partial T)_P$.

- <u>Ratio of specific heats</u> $\gamma = c_P/c_V = C_P/C_V$.
- For a reversible process, $dU = dQ_r PdV$.
- For an adiabatic process, $dQ_r = 0$, so that dU = -P dV.
- For an ideal gas, U = U(T), so that $C_V = dU/dT$. Also, PV = nRT and H = U + PV, so that H =H(T). Thus, H = H(T) and $C_P = dH/dT$.
- Thus, $C_P C_V = dH/dT dU/dT = d(PV)/dT = nR$.
- C_P C_V = nR is known as *Mayer's Equation*, which holds for an ideal gas only.
- For 1 kmole, $c_P c_V = R$, where c_P and c_V are specific heats.

- Since dQ = 0 for an adiabatic process, dU = -P dV and $dU = C_V dT$, so that $dT = -(P/C_V) dV$.
- For an ideal gas, PV = nRT, so that P dV +V dP = nR dT = - (nRP/C_v) dV.
 - Hence V dP + P $(1 + nR/C_v)$ dV = 0.

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Thus, C_v dP/P + (C_v + nR) dV/V = 0.
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For an ideal gas, C_P - C_V = nR.
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so that $C_V dP/P + C_P dV/V = 0$, or $dP/P + \gamma dV/V = 0$.

• Integration gives $\ln P + \gamma \ln V = \text{constant}$, so that

 $PV^{\gamma} = constant.$

- Work done in a reversible adiabatic process
- Method 1: direct integration
- For a reversible adiabatic process, $PV^{\gamma} = K$.
- Since the process is reversible, $W = \int PdV$, so that $W = K \int V^{-\gamma} dV = -[K/(\gamma - 1)] V^{-(\gamma - 1)} |_{V_1}^{V_2}$ $= -[1/(\gamma - 1)] PV |_{P_1V_1}^{P_2V_2}$

:
$$W = - [1/(\gamma - 1)] [P_2V_2 - P_1V_1].$$

• For an ideal monatomic gas, $\gamma = 5/3$, so that $W = -(3/2) [P_2V_2 - P_1V_1].$

- Work done in a reversible adiabatic process
- Method 2: from 1st Law
- For a reversible process, $W = Q_r \Delta U$ so that $W = -\Delta U$, since $Q_r = 0$ for an adiabatic process. For an ideal gas, $\Delta U = C_V \Delta T = nc_V \Delta T = nc_V (T_2 - T_1)$. Thus, $W = -nc_V (T_2 - T_1)$.
- For an ideal gas PV = nRT, so that $W = -(c_V/R)[P_2V_2 - P_1V_1]$.
- But $R = c_P c_V$ (Mayer's relationship for an ideal gas), so that $W = - [c_V/(c_P - c_V)][P_2V_2 - P_1V_1]$

i.e.
$$W = -[1/(\gamma - 1)] [P_2V_2 - P_1V_1].$$

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Reversible Processes for an Ideal Gas

Adiabatic process	Isothermal process	Isobaric process	Isochoric process
$PV^{\gamma} = K$ $\gamma = C_P/C_V$	T constant	P constant	V constant
$W = - [1/(\gamma - 1)]$ $.[P_2V_2 - P_1V_1]$	$W = nRT \ln(V_2/V_1)$	$W = P \Delta V$	W = 0
$\Delta U = C_V \Delta T$	$\Delta U = 0$	$\Delta U = C_V \Delta T$	$\Delta U = C_V \Delta T$

PV = nRT, U = nc_VT , $c_P - c_V = R$, $\gamma = c_P/c_V$. Monatomic ideal gas $c_V = (3/2)R$, $\gamma = 5/3$.

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The Fundamental Thermodynamic Relation

- The 1st Law, dU = dQ dW, relates an exact differential, dU, to the difference between two inexact differentials.
- The change in a state function depends only on the initial and final states (ΔU = U₂ – U₁), and is independent of path, while Q and W are each dependent on path (although the difference between them must be path-independent).
- The right-hand-side of the differential form of the 1st Law must be replaceable by an expression containing only state functions.
- This is done through the equation known variously as the fundamental thermodynamic relation, the thermodynamic identity, or the central equation of thermodynamics:

dU = T dS - P dV.

The Entropy

- The entropy S is introduced through the fundamental relation: dU = TdS – PdV, where (TdS – PdV) equals (dQ – dW) of the 1st Law.
- Only for a <u>reversible</u> process (r) can the individual terms be equated: i.e.

 $dQ_r = TdS$, $dW_r = PdV$.

• In general,

 $dQ \leq TdS$, $dW \leq PdV$,

where the equality sign refers to a reversible process.

- Examples of irreversible changes are the following:
 - i. a free adiabatic expansion (for $dQ \le TdS$);
 - ii. a piston with friction (for $dW \le PdV$).
Second Law of Thermodynamics 1

• The entropy of an isolated system never decreases; i.e. $\Delta S \ge 0$.

or, at equilibrium, $S \rightarrow S_{max}$.

• For a reversible (idealized) process only,

 $\Delta S = 0$, dS = dQ/T.

- Examples of irreversible (real) processes:
- i. temperature equalization;
- ii. mixing of gases;
- iii. conversion of macroscopic (ordered) KE to thermal (random) KE.

The last two cases are obvious examples of the association of entropy with disorder.

Second Law of Thermodynamics 2

- Features of the Entropy
- It is a state function, so that ΔS between given states is independent of path.
- It is a quantitative measure of the disorder of a system.
- It gives a criterion for the direction of a process, since an isolated system will reach a state of maximum entropy.
- ΔS may be negative for a portion of a composite system.
- An increase of entropy does not require an increase of temperature; e.g. in the mixing of gases at the same temperature, or in the melting of a solid at the melting point.
- An increase of temperature does not necessarily imply an increase of entropy; e.g. in the adiabatic compression of a gas.

The 2nd Law and Life on Earth 1

- The existence of low-entropy organisms like ourselves has sometimes been used to suggest that we live in violation of the 2nd Law.
- Sir Roger Penrose has considered our situation in his monumental work "The Road to Reality: a Complete Guide to the Laws of the Universe" (2005).
- In it, he points out that it is a common misconception to believe that the Sun's energy is the main ingredient needed for our survival. However, what is important is that the energy source be far from thermal equilibrium. For example, a uniformly illuminated sky supplying the same amount of energy as the Sun, but at a much lower energy, would be useless to us.
- Fortunately the Sun is a hot sphere in an otherwise cold sky.
- It is a low entropy source, which keeps our entropy low. ³⁹

The 2nd Law and Life on Earth 2



- The optical photons supplied by the Sun contain much more energy than the IR photons leaving us, since $\varepsilon_{ph} = hv$.
- Since the energy the energy reaching us is contained in fewer photons, the Sun is a low entropy source.
- Plants utilize the low entropy energy, to reduce their entropy through *photosynthesis*.
- We keep our entropy low by breathing oxygen produced by plants, and by eating plants, or animals ultimately dependent on plants.

Increasing Entropy: No Gravity & Gravity



- Without gravity, entropy increases as the gas spreads out.
- When gravity is present, clumping increases the entropy, which changes enormously with the formation of black holes.

Entropy Changes: Reversible Processes 1

In General

$$\begin{split} dS &= dQ_r/T = dU/T + P \; dV/T = C_V(T) \; dT/T + P \; dV/T \; . \\ \underline{Special \; case: \; any \; ideal \; gas} \\ dU &= C_V dT \; , \quad PV = nRT \; . \\ Thus, \; \Delta S \; = \; C_V \int dT/T \; + \; nR \; \int dV/V \\ &= C_V \; ln(T_2/T_1) \; + \; nR \; ln(V_2/V_1). \\ \underline{Special \; case: \; ideal \; monatomic \; gas} \\ & C_V = (3/2) \; nR \; . \\ Thus, \; \Delta S \; = \; nR \; \{ln[(T_2/T_1)^{3/2}(V_2/V_1)]\}, \\ & \text{ or } \; \Delta S \; = \; nR \; ln(T^{3/2}V) \; + \; constant. \end{split}$$

Adiabatic process: $\Delta S = \int dQ_r/T = 0$, since $dQ_r = 0$. Phase change: $\Delta S = Q/T = L_i/T$. Isochoric process (ideal gas): $\Delta S = C_V \ln(T_2/T_1)$. Isobaric process (ideal gas): $\Delta S = C_P \ln(T_2/T_1)$.

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Entropy Changes: Reversible Processes 2



V

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 $V_3/T_3 = V_2/T_2 = V_2/T_1.$

Entropy Changes: Irreversible Processes 1

- Free adiabatic expansion of a gas (into a vacuum)
- This is the Joule process, for which Q, W and ΔU are all zero.
- Ideal gas : U = U(T), so that $\Delta T = 0$.
- Since the final equilibrium state is that which would have been obtained in a reversible isothermal expansion to the same final volume,

$$\Delta S = nR \ln(V_2/V_1).$$

- Remember, that the entropy is a state function, so that its change depends only on the initial and final states, and <u>not</u> on the process.
- <u>Real (non-ideal) gas</u>: $\Delta U = \Delta(KE) + \Delta(PE) = 0$.
- Since the intermolecular PE increases with increasing volume, Δ (KE) decreases, so that the temperature decreases. 44

Entropy Changes: Irreversible Processes 2

- Let the system have initial temperature T₁ and entropy S(T), and the reservoir have temperature T₀ and entropy S₀.
- For the system, $Q = \int C(T) dT$ and $\Delta S = \int dQ/T = \int [C(T)/T] dT$.
- For the bath, $Q_0 = -Q = -\int C(T) dT$ and $\Delta S_0 = -Q/T_0$.
- <u>Special case</u>: constant C. $C \int dT/T = C \ln(T_0/T_1),$ $\Delta S_0 = -Q/T_0 = -C(T_0 - T_1)/T_0 = C[(T_1/T_0) - 1].$ $\Delta S_{univ} = \Delta S + \Delta S_0$ $= C [\ln(T_0/T_1) + (T_1/T_0) - 1]$ $= C(T_1/T_0)f(x),$ where f(x) = x lnx + 1 - x, and x = T_0/T_1. From this result, we may show that $\Delta S_{univ} > 0$ for $T_1 \neq T_0$.

Three Types of Expansion

Isothermal expansion



 $\frac{\text{Ideal gas}}{\Delta S = nR \ln(V_2/V_1)}.$

Adiabatic expansion



 $\frac{\text{Any gas}}{\Delta S = 0}.$

(Adiabatic) free expansion



Adiabatic wall $\frac{\text{Ideal gas}}{\Delta S = nR \ln(V_2/V_1).}$

Comparison of Three Types of Expansion

			Adiabatic*	Isothermal*	Free**
Universe	General	ΔS	0	0	+
Surroundings	General	ΔS	0	_	0
System	General	ΔS	0	+	+
		Q	0	+	0
		W	+	+	0
System	Ideal gas	ΔU	_	0	0
		ΔΤ	—	0	0
System	Real gas	ΔU	_	+	0
		$\Delta(PE)$	+	+	+
		$\Delta(KE)$	—	0	—
		ΔΤ	_	0	—

* Signs are reversed for contractions.

** There is no reverse process for a free expansion.

2nd Law: Clausius and Kelvin Statements





- Clausius statement (1850)
- Heat cannot by itself pass from a colder to a hotter body; i.e. it is impossible to build a "perfect" refrigerator.
- The hot bath gains entropy, the cold bath loses it.

 $\Delta S_{univ} = Q_2/T_2 - Q_1/T_1 = Q/T_2 - Q/T_1 < 0.$

- Kelvin statement (1851)
- No process can completely convert heat into work; i.e. it is impossible to build a "perfect" heat engine.

 $\Delta S_{univ} = - Q/T < 0.$

- 1st Law: one cannot get something for nothing (energy conservation).
- 2nd Law: one cannot even break-even (efficiency must be less than unity). 48

Cyclic Heat Engine

Second Law

 $\Delta S_{univ} = \Delta S + \Delta S' \ge 0$, where S and S' are the entropies of the system and surroundings respectively.

• After one cycle,

$$\begin{split} \Delta S_{univ} &= \Delta S' = - \operatorname{Q}_2/\operatorname{T}_2 + \operatorname{Q}_1/\operatorname{T}_1 \geq 0, \\ \text{so that} \qquad \operatorname{Q}_1/\operatorname{Q}_2 \geq \operatorname{T}_1/\operatorname{T}_2. \end{split}$$

Also
$$\Delta U = 0$$
, so that $Q_2 - Q_1 = W$,

Efficiency

 $\eta = W/Q_2 = 1 - Q_1/Q_2$. Thus, the maximum efficiency for a reversible or Carnot engine is n - 1 - T/T

 $\eta_r = 1 - T_1/T_2.$



Reversible Engine: the Carnot Cycle



Since $Q_1/Q_2 = T_1/T_2$, $\eta = \eta_r = 1 - T_1/T_2$.

- <u>Stage 1</u> Isothermal expansion at temperature T₂, while the entropy rises from S₁ to S₂.
- The heat <u>entering</u> the system is $Q_2 = T_2(S_2 - S_1).$
- <u>Stage 2</u> adiabatic (isentropic) expansion at entropy S₂, while the temperature drops from T₂ to T₁.
- <u>Stage 3</u> Isothermal compression at temperature T₁, while the entropy drops from S₂ to S₁.
- The heat l<u>eaving</u> the system is $Q_1 = T_1(S_2 - S_1).$
- <u>Stage 4</u> adiabatic (isentropic) compression at entropy S₁, while the temperature rises from T₁ to T2. 50

Maxwell's relations: table

Internal energy	<i>S</i> , <i>V</i>	$T = \left(\frac{\partial U}{\partial S}\right)_{V}$	$\left(\frac{\partial T}{\partial V}\right)_{S} = -\left(\frac{\partial P}{\partial S}\right)_{V}$
U	$dU = T \ dS - P \ dV$	$-P = \left(\frac{\partial U}{\partial V}\right)_{S}$	
Enthalpy	<i>S</i> , <i>P</i>	$T = \left(\frac{\partial H}{\partial S}\right)_P$	$\left(\frac{\partial T}{\partial P}\right)_{S} = \left(\frac{\partial V}{\partial S}\right)_{P}$
H = U + PV	$dH = T \ dS + V \ dP$	$V = \left(\frac{\partial H}{\partial P}\right)_{S}$	
Helmholtz function	<i>T</i> , <i>V</i>	$S = -\left(\frac{\partial F}{\partial T}\right)_{V}$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
F = U - TS	dF = -S dT - P dV	$-P = \left(\frac{\partial F}{\partial V}\right)_T$	5.
Gibbs function	<i>T</i> , <i>P</i>	$S = -\left(\frac{\partial G}{\partial T}\right)_P$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$
G = U - TS + PV $= H - TS$	dG = -SdT + V dP	$V = -\left(\frac{\partial G}{\partial P}\right)_T$	
= F + PV			

Maxwell Relation for G

The Gibbs function (or free energy) is defined as G = U - TS + PV $\therefore dG = dU - TdS - SdT + PdV + Vdp .$ dU = TdS - PdV,so that dG = -SdT + VdP; i.e. G = G(T,P).

> $dG = (\partial G/\partial T)_P dT + (\partial G/\partial P)_T dP,$ so that S = - ($\partial G/\partial T$)_P and V = ($\partial G/\partial P$)_T...

> > $\partial^2 G / \partial T \partial P = \partial^2 G / \partial P \partial T,$ so that $(\partial S / \partial P)_T = -(\partial V / \partial T)_P$.

Note that Maxwell's relation equates $(\partial S/\partial P)_T$, a theoretical quantity, to $(\partial V/\partial T)_P = V\beta$, both of which may be measured.

Adiabatic Free Expansion: Joule effect

The Joule effect is the adiabatic free expansion of a gas jnto a vacuum, which will cool a real (non-ideal) gas.



 $Q = 0, W = 0, \therefore \Delta U = 0$ (1st Law).

For an ideal gas, U = U(T), so that $\Delta T = 0$.

<u>Joule coefficient</u> $\alpha_J = (\partial T / \partial V)_U$ is <u>negative</u> for cooling.

 $\begin{array}{l} (\partial T/\partial V)_U &= - \ (\partial T/\partial U)_V \ (\partial U/\partial V)_T = - \ (\partial U/\partial V)_T/C_V.\\ \text{Now } \Delta U &= T \ \Delta S - P \ \Delta V \ \therefore \ (\partial U/\partial V)_T = T \ (\partial S/\partial V)_T - P.\\ \text{Maxwell's relations give } \ (\partial S/\partial V)_T = (\partial P/\partial T)_V, \text{ so that}\\ \alpha_J &= \ (\partial T/\partial V)_U = - \ [T(\partial P/\partial T)_T - P]/C_V. \end{array}$

Equilibrium when $T_i = T_f$ and $V_i = V_f$.

- Consider a constant-volume system in contact with a heat bath.
- The 1st Law gives $W = -\Delta U + Q < -\Delta U + T \Delta S.$

Now F = U – TS

 $\therefore \Delta F = \Delta U - T \Delta S$ (for constant T).

Thus, $W < -\Delta F$.

Since V is constant, W = 0, so that

 $(\Delta F)_{T,V} < 0$, or $F \rightarrow F_{min}$.



Since F is a state function, T and V do <u>not</u> have to be constant during the process, as long as $T_i = T_f$ and $V_i = V_f$. ⁵⁴

Equilibrium when $T_i = T_f$ and $P_i = P_f$.

- Consider a constant-pressure system in contact with a heat bath.
- The 1st Law gives

 $W = -\Delta U + Q < -\Delta U + T \Delta S.$

- For reversible work, $W = P \Delta V$, so that $P \Delta V < -\Delta U + T \Delta S$, or $0 > \Delta U + P \Delta V - T \Delta S$.
- Now G = U + PV TS,

$$\therefore \Delta G = \Delta U + P \Delta V - T \Delta S$$
 for constant

T and P, so that

$$(\Delta G)_{T,P} < 0, \text{ or } G \rightarrow G_{min}$$



Since G is a state function, T and P do <u>not</u> have to be constant during the process, as long as $T_i = T_f$ and $P_i = P_f$.⁵⁵

Joule-Thomson Effect: Throttling process



- The Joule-Thomson effect is a continuous process in which the wall temperatures remain constant after equilibrium is reached.
- For a given mass of gas, $W = P_2V_2 P_1V_1$.
- Since $\Delta U = Q W$, qnd Q = 0, $U_2 U_1 = -(P_2V_2 P_1V_1)$.
- Thus $U_2 + P_2V_2 = U_1 + P_1V_1$, so that $H_2 = H_1$ or $\Delta H = 0$.
- Joule-Thomson coeff. $\alpha_{JT} = (\partial T / \partial P)_H$ is positive for cooling.
- $(\partial T/\partial P)_{H} = -(\partial T/\partial H)_{P} (\partial H/\partial P)_{T} = -(\partial H/\partial P)_{T}/C_{P}$.
- Now $\Delta H = T \Delta S + V \Delta P$: $(\partial H/\partial P)_T = T(\partial S/\partial P)_T + V$.
- Maxwell's relations give $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$, so that

 $\alpha_{JT} = (\partial T / \partial P)_{H} = [T (\partial V / \partial T)_{T} - V] / C_{P}$.

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Second Virial Coefficient



 For one kmole, the equation of state may be written as Pv = RT [1 + (B₂/v) + (B₃/v²) +....], where B_i(T) is the i'th *virial coefficient*.

At sufficiently low densities $P \approx (RT/v)[1 + (B_2/v)]$, where B_2 is negative at low, and positive at high temperatures, and dB_2/dT is positive.

Joule-Thomson Effect in Terms of B₂

- Using the approximation for very low densities
 P ≈ (RT/v)[1 + (B₂/v)] ≈ (RT/v)[1 + (PB₂/RT)],
 where 1/v was replaced by P/RT in the second term.
- Thus, $v = (RT/P) + B_2$, and $(\partial v/\partial T)_P = (R/P) + dB_2/dT$, so that $= (\partial T/\partial P)_H = [T(\partial v/\partial T)_T - v]/c_P$; i.e. $\alpha_{JT} = [T(dB_2/dT) - B_2]/c_P$.

<u>Low temperatures</u> B_2 is negative and dB_2/dT is positive, so that α_{JT} is positive and <u>cooling</u> occurs.

Intermediate temperatures B_2 is positive, but less than dB_2/dT , so that α_{JT} is positive and <u>cooling</u> occurs

<u>High temperatures</u> B_2 is positive, but greater than dB_2/dT , so that α_{JT} is negative and <u>warming</u> occurs.

The Linde Process of Liquefaction



Comparison of U and H

	Internal Energy U	Enthalpy H = U + PV
Always true	dU = T dS - P dV	dH = T dS + V dP
Reversible procedure	dU = dQ – P dV	dH = dQ + V dP
Heat capacity	$C_v = (\partial U / \partial T)_v$	C _P = (∂H∂/T) _P
	= T(∂S/∂T) _V	= T(∂S/∂T) _P
Ideal gas	$U = U(T), \Delta U = C_{V} \Delta T$	H = H(T)
Isochoric process	∆U = Q = ∫C _v (T) dT	∆H = Q = ∫C _P (T) dT
Adiabatic process	∆U = – ∫P dV	∆H = ∫V dP
Joule & J-T effects	$\alpha_{J} = -[T(\partial P/dT)_{V} - P]/C_{V}$	$\alpha_{JT} = + \left[T(\partial V/dT)_{P} - \sqrt[60]{C_{P}} \right]$

Difference of Heat Capacities

In general, $S = S(T,P) \therefore dS = (\partial S/\partial T)_P dT + (\partial S/\partial P)_T dP$. Now $C_V = T(\partial S/\partial T)_V$, $C_P = T(\partial S/\partial T)_P$, and $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$ So that $TdS = C_P dT - T(\partial V/\partial T)_P dP$.

Now, $C_V = T(\partial S/\partial T)_V = C_P - T(\partial V/\partial T)_P (\partial P/\partial T)_V$. Since $(\partial P/\partial T)_V = -(\partial P/\partial V)_T (\partial V/\partial T)_P$, $C_P = C_V - T(\partial V/\partial T)_P^2 (\partial P/\partial V)_T$. Now, $\beta = (\partial V/\partial T)_P / V$ and $\kappa_T = -(\partial V/\partial P)_T / V$, so that $C_P = C_V + TV\beta^2/\kappa$.

<u>Notes</u>

i. For an ideal gas, $C_P = C_V + nR$ (Mayer's equation).

ii. $C_P \ge C_V$, with $C_P = C_V$ only if $\beta = 0$ (e.g water at 3.98°C).⁶¹

Phase Equilibrium in a One-component System

- Consider a system at constant T and P, so that $G \rightarrow G_{min}$ at equilibrium, so that dG = 0.
- Let g₁ and g₂ be the specific Gibbs functions of the phases 1 and 2, with n₁ + n₂ = n (which is constant).
- $G = n_1g_1 + n_2g_2$, so that $G = G(T, P, n_1, n_2)$, Thus, $dG = [(\partial G/\partial T)dT + (\partial G/\partial P)dP + (\partial G/\partial n_1)dn_1 + (\partial G/\partial n_2)dn_2]$.
- Now dT = dP = 0, and $(\partial G/\partial n_i) = g_i(T,P)$, where i =1 or 2.
- At equilibrium, dG = 0, so that $0 = g_1 dn_1 + g_2 dn_2$, Since n is constant, $dn_1 = -dn_2$, so that $g_1 = g_2$.
- This equation defines a phase-equilibrium curve.

Phase Equilibrium Curve 1



Clausius-Clapeyron Equation 1



Clausius-Clapeyron Equation 2

<u>Vapor pressure curve</u>

 $dP/dT = \Delta s/\Delta v = I_v(T,P)/T\Delta v$, where $\Delta v = v_v - v_L$.

1st assumption

 $v_v \gg v_L$, so that $\Delta v \approx v_v$, and $dP/dT \approx I_v/Tv_v$.

<u>2nd assumption</u>

Assume ideal gas behavior (Pv = RT), and a latent heat I_v that depends only on temperature, so that

$$\label{eq:dPdT} \begin{split} dP/dT &\approx I_V/Tv_V \approx I_V(T)/(RT^2/P) = PI_V(T)/(RT^2). \\ Thus, \ensuremath{\int} dP/P &= \ln(P/P_0) \approx \ensuremath{\int} L_V(T) \ dT/(RT^2). \end{split}$$

• <u>3rd assumption</u> Assume L_V(T) is a constant, so that $ln(P/P_0) \approx (l_V/R) \int dT/T^2 = (l_V/R)[(1/T_0) - (1/T)].$ Thus, P ≈ P₀ exp{(l_V/R)[(1/T₀) - (1/T)]}.

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- For a first-order phase transition, discontinuities occur in both s and v, the former giving rise to the latent heat.
- For most materials, Δs and Δv are both positive in going from solid to liquid; water is an exception.

All Liquids Banned from Airlines!



 For the first time, the Department of Homeland Security has deemed an entire state of matter to be a national security risk.

Enthalpy and Change of Phase

- Consider a <u>reversible phase-change</u> at constant T and P, which is associated with a latent heat L.
- The 1st Law, $\Delta U = Q W$, may be written as $\Delta U = L P\Delta V$.

• Thus,
$$U_2 - U_1 = L - P(V_2 - V_1)$$
,
so that

$$L = (U_2 + PV_2) - (U_1 + PV_1).$$

• But the enthalpy H = U + PV, so that

$$\mathsf{L} = \mathsf{H}_2 - \mathsf{H}_1.$$

 Since U, P and V are functions of state, H must also be a function of state, so that

Latent Heats at the Triple Point



- Consider a cyclic process around and close to the triple point.
- L_s (sublimation) = $H_v H_s$,
- L_F (fusion) = $H_I H_s$,
- L_v (vaporization) = $H_v H_l$, where I is liquid, s is solid and v is vapor.
- Since $\int dH = 0$,
 - $L_{S} = L_{F} + L_{V}.$
 - Also, $g_s = g_l = g_v$. 69

Entropy of EM Radiation 1

- Internal energy U(V,T) = V u(T), where u(T) is the energy density, so that dU = V du + u dV.
- From EM theory, the radiation pressure is given by P = u(T)/3.

Let
$$S = S(T,V)$$
 $\therefore dS = \left(\frac{\partial S}{\partial T}\right)_{V} dT + \left(\frac{\partial S}{\partial V}\right)_{T} dV$.
From above $dS = \stackrel{\vee}{T} \frac{\partial u}{\partial T} dT + \stackrel{\omega}{T} \frac{\partial V}{\partial T} dV$,
 $\therefore \left(\frac{\partial S}{\partial T}\right)_{V} = \stackrel{\vee}{T} \frac{\partial u}{\partial T}$, $\left(\frac{\partial S}{\partial V}\right)_{T} = \stackrel{\omega}{T} \frac{\omega}{T}$.

Entropy of EM Radiation: Stefan-Boltzmann Law

Entropy of EM radiation

$$\left(\frac{\partial S}{\partial V}\right)_{T} = \frac{4}{3}\frac{\mu}{T} \quad \therefore \quad \Delta S = \left(\frac{4\pi}{3}\frac{\mu}{T}\partial V\right) = \frac{4\pi}{3}\frac{\mu V}{T} + f(T)$$

$$T_{const}$$
But S is an extensive quantity, proportional to V
$$so \quad that \quad f(T) = 0.$$

$$Thus \quad S = \frac{4\pi}{3}\frac{\mu V}{T} = \frac{4\pi}{3}a T^{3}V.$$

Stefan-Boltzmann Law

$$\begin{array}{ccc} & \left(\frac{\partial S}{\partial T}\right)_{V} = \frac{V}{T} \frac{du}{dT} & \left(\frac{\partial S}{\partial V}\right)_{T} = \frac{4}{3} \frac{u}{T} \\ & \left(\frac{\partial^{2} S}{\partial V}\right)_{T} = \frac{1}{T} \frac{du}{dT} & \left(\frac{\partial^{2} S}{\partial T}\right)_{T} = \frac{4}{3} \frac{1}{T} \frac{du}{dT} - \frac{4}{3} \frac{u}{T^{2}} \\ & \left(\frac{\partial^{2} S}{\partial V}\right)_{T} = \frac{4}{3} \frac{1}{T} \frac{du}{dT} - \frac{4}{3} \frac{u}{T^{2}} \\ & \left(\frac{\partial^{2} S}{\partial V}\right)_{T} = \frac{4}{3} \frac{1}{T} \frac{du}{dT} - \frac{4}{3} \frac{u}{T^{2}} \\ & \left(\frac{\partial^{2} S}{\partial V}\right)_{T} = \frac{4}{3} \frac{1}{T} \frac{du}{dT} - \frac{4}{3} \frac{u}{T^{2}} \\ & \left(\frac{\partial^{2} S}{\partial V}\right)_{T} = \frac{4}{3} \frac{1}{T} \frac{du}{dT} - \frac{4}{3} \frac{u}{T^{2}} \\ & \left(\frac{\partial^{2} S}{\partial V}\right)_{T} = \frac{4}{3} \frac{1}{T} \frac{du}{dT} - \frac{4}{3} \frac{u}{T^{2}} \\ & \left(\frac{\partial^{2} S}{\partial V}\right)_{T} = \frac{4}{3} \frac{1}{T} \frac{du}{dT} - \frac{4}{3} \frac{u}{T^{2}} \\ & \left(\frac{\partial^{2} S}{\partial V}\right)_{T} = \frac{4}{3} \frac{1}{T} \frac{du}{dT} \\ & \left(\frac{\partial^{2} S}{\partial T}\right)_{T} = \frac{4}{3} \frac{1}{T} \frac{du}{dT} \\ & \left(\frac{\partial^{2} S}{\partial T}\right)_{T} = \frac{4}{3} \frac{1}{T} \frac{du}{dT} \\ & \left(\frac{\partial^{2} S}{\partial T}\right)_{T} = \frac{4}{3} \frac{1}{T} \frac{du}{dT} \\ & \left(\frac{\partial^{2} S}{\partial T}\right)_{T} = \frac{4}{3} \frac{1}{T} \frac{du}{dT} \\ & \left(\frac{\partial^{2} S}{\partial T}\right)_{T} \\ & \left(\frac{\partial^{2} S}{\partial T}\right)_{T} = \frac{4}{3} \frac{1}{T} \frac{du}{dT} \\ & \left(\frac{\partial^{2} S}{\partial T}\right)_{T} = \frac{4}{3} \frac{1}{T} \frac{du}{dT} \\ & \left(\frac{\partial^{2} S}{\partial T}\right)_{T} \\ & \left(\frac{\partial^{2} S}{\partial$$

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Third Law of Thermodynamics

• The 3rd Law fixes the absolute value of the entropy; i.e.

$$S \rightarrow 0 \text{ as } T \rightarrow 0.$$

Reif's practical statement is

$$S \rightarrow S_0 \text{ as } T \rightarrow 0_+,$$

where 0_+ , is of the order of 0.1 K, which is low enough for the electronic system to be in its ground state ($S_{elec} \rightarrow 0$), but high enough for the nuclear spin system to have its high T value.



The unattainability of absolute zero

Because of the 3rd Law, entropytemperature curves for a fixed external parameter, such as magnetic field, meet at $T \rightarrow 0$.

Thus, it is impossible to reach T = 0in a finite number of steps.
Consequences of the 3rd Law
1.
$$C_i \rightarrow 0$$
 as $T \rightarrow 0$, at least as fast as T^* , where $x = 1$
 $\Delta s = \int \frac{d\Theta}{T} = \int c_i(T) \frac{dT}{T} \therefore S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{c_i(T)}{T} dT_1$
As $T_i \rightarrow 0$, $\int_{T_1}^{T_2} \frac{c_i(T)}{T}$ must remain finite.

• Thus, $C_i(T)$ cannot vary by a power of T, which is less than one. 2. $(\partial P/\partial T)_v$ and $(\partial P/\partial T)_P \rightarrow 0$ as $T \rightarrow 0$.

$$\begin{pmatrix} \frac{\partial P}{\partial T} \end{pmatrix}_{U} = \begin{pmatrix} \frac{\partial s}{\partial U} \end{pmatrix}_{T} \rightarrow 0 \quad \text{as} \quad T \rightarrow 0 .$$

$$\begin{pmatrix} \frac{\partial U}{\partial T} \end{pmatrix}_{p} = -\begin{pmatrix} \frac{\partial s}{\partial P} \end{pmatrix}_{T} \rightarrow 0 \quad \text{as} \quad T \rightarrow 0 .$$

$$\therefore f^{3} = \frac{1}{U} \begin{pmatrix} \frac{\partial U}{\partial T} \end{pmatrix}_{p} \rightarrow 0 \quad \text{as} \quad T \rightarrow 0 .$$

$$\text{Nobe} : \mathcal{M}_{T} = \frac{1}{U} \begin{pmatrix} \frac{\partial U}{\partial P} \end{pmatrix}_{T} \text{ remains finite} .$$

$$3. \left(\frac{C_{p} - C_{v}}{C_{v}} \right) C_{v} \rightarrow 0 \text{ as } T \rightarrow 0 .$$

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Experimental Test of 3rd Law (Lange, 1924)

- Grey tin, a semiconductor, is stable below $T_0 = 292$ K.
- White tin, a metallic conductor, is stable above T₀.
- The rapid cooling of white tin to below T₀ results in the formation of a metastable state of white tin;

$$S_{\omega}(T_{o}) - S_{g}(T_{o}) = 1/T_{o},$$
where the lotent heat per kmole = 2240 kJ.
By the 3rd Law, $S_{\omega}(0) - S_{g}(0) = 0$
Thus $\left[S_{\omega}(T_{o}) - S_{\omega}(0)\right] - \left[S_{g}(T_{o}) - S_{g}(0)\right] = \frac{1}{T_{o}}$
as $\int_{0}^{T_{o}} \left[c_{\omega}(T) - c_{g}(T)\right] \frac{dT}{T} = \frac{1}{T_{o}}$

• $c_w(T)$ and $c_g(T)$ must be measured between 0+ and T_0 . ⁷⁴