

Thermodynamic Laws

0th: “If two systems are in thermal equilibrium with a third system, they are in thermal equilibrium with each other” Introduces the thermodynamic intensive variable of temperature (T)

1st: “When energy passes, as work, as heat, or with matter, into or out from a system, the

system's internal energy changes in accord with the law of conservation of energy”

Conservation and conversion of energy: Defines extensive thermodynamic state variable of internal energy (U) $dU = \delta q - \delta w$ or $\Delta U = Q - W$

2nd: “In a natural thermodynamic process, the sum of the entropies of the interacting

thermodynamic systems increases” Defines the extensive thermodynamic state variable of entropy (S) $dS_{universe} \geq 0$

3rd: “The entropy of a system approaches a constant value as the temperature approaches

absolute zero” For systems in internal equilibrium, sets the zero of entropy at minimum in temperature (0K) and at the minimum in internal energy.

Mathematical Transforms

$$\text{For } X = X(Y, Z) \Rightarrow dX = \left(\frac{\partial X}{\partial Y}\right)_Z dY + \left(\frac{\partial X}{\partial Z}\right)_Y dZ$$

$$\text{For } X = X(Y, Z) \Rightarrow \left(\frac{\partial X}{\partial Y}\right)_Z = \left(\frac{\partial Y}{\partial X}\right)_Z^{-1} = \frac{1}{\left(\frac{\partial Y}{\partial X}\right)_Z}$$

$$\text{For } X = X(Y, Z) \Rightarrow \left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X \left(\frac{\partial Z}{\partial X}\right)_Y = -1$$

$$\text{For } N = N(X, Y, Z) \text{ and } X \& Y \text{ are the independent} \Rightarrow \left(\frac{\partial N}{\partial X}\right)_Z = \left(\frac{\partial N}{\partial X}\right)_Y + \left(\frac{\partial N}{\partial Y}\right)_X \left(\frac{\partial Y}{\partial X}\right)_Z$$

$$\text{For } N = N(X, Y, Z) \text{ and } X \& Y \text{ are the independent} \Rightarrow \left(\frac{\partial N}{\partial Y}\right)_Z = \left(\frac{\partial N}{\partial X}\right)_Z \left(\frac{\partial X}{\partial Y}\right)_Z$$

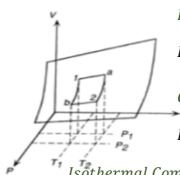
$$\text{For } X = X(Y, Z) \Rightarrow dX = \left(\frac{\partial X}{\partial Z}\right)_Y dZ + \left(\frac{\partial X}{\partial Y}\right)_Z dY = \left(\frac{\partial X}{\partial Z}\right)_Y dZ + \left(\frac{\partial X}{\partial Y}\right)_Z dY$$

$$dH = TdS + VdP + Xdy; dA = -SdT - PdV + Xdy; dG = -SdT + VdP + Xdy$$

$$\text{When } X > 1000 \Rightarrow \ln X \approx X \ln X - X + \ln(2\pi N)^{\frac{1}{2}}; \ln X \approx X \ln X - X$$

$$\text{For small } x \Rightarrow e^x = (1 + x); \text{ for small } x \Rightarrow e^{-x} = (1 - x)$$

State Functions



$$\text{Path } 1 \rightarrow a \rightarrow 2 \Rightarrow \Delta V = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T}\right)_{P_1} dT + \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P}\right)_{T_2} dP$$

$$\text{Path } 1 \rightarrow b \rightarrow 2 \Rightarrow \Delta V = \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P}\right)_{T_1} dP + \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T}\right)_{P_2} dT$$

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

$$\text{Rewritten as: } dV = -\beta V_0 dP + \alpha V_0 dT$$

$$\text{Isothermal Compressibility } \beta \text{ with dimensions } P^{-1}: \beta = -\frac{1}{V_0} \left(\frac{\partial V}{\partial P}\right)_T$$

$$\text{Coefficient of thermal expansion with dimensions } T^{-1}: \alpha = \frac{1}{V_0} \left(\frac{\partial V}{\partial T}\right)_P$$

$$\text{Thermal coefficient of pressure with dimensions } T^{-1}: \gamma = \frac{1}{P_0} \left(\frac{\partial P}{\partial T}\right)_V$$

Processes: Constraints

Isobaric (same pressure): $dp = 0$

Isothermal (fixed temperature): $dT = 0$

Isochoric (fixed volume): $dV = 0$

Adiabatic (q does not go in or out): $\delta q = 0$

Cyclic (all state variables): $\Delta = 0$

Heat Capacity (C) - ratio of thermal energy added to or withdrawn from a system (of fixed composition) to the resultant change in the temperature of the system $C \equiv \frac{q}{\Delta T}$ or $C \equiv \frac{\delta q}{dT}$

Heat Capacity is path dependent: $C_V = \left(\frac{\delta q}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V$ or $dU' = C_V dT$; $C_V = nc_V$

also: $C_P = \left(\frac{\delta q}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P$ or $dH' = C_P dT$; $C_P = nc_P$ and $C_P > C_V$

per mole: $c_P - c_V = P \left(\frac{\partial V}{\partial T}\right)_P = P \frac{V}{T} = \frac{RT}{T} = R$

	C_V	C_P
1	$\frac{3}{2}R$	$\frac{5}{2}R$
2	$\frac{5}{2}R$	$\frac{7}{2}R$

More exactly: $C_P - C_V = \left[\left(\frac{\partial U'}{\partial V'}\right)_T + P\right] \left(\frac{\partial V'}{\partial T}\right)_P$

The two expressions for the difference in heat capacities are equal if $\left(\frac{\partial U'}{\partial V'}\right)_T = 0$. This is true for an ideal gas in which U' is not a function of V' , that is $U' = U'(T)$

Reversible Adiabatic $\Delta U = -w = c_V \Delta T$

$$c_V \ln \left(\frac{T_2}{T_1}\right) = R \ln \left(\frac{V_2}{V_1}\right) \Rightarrow \left(\frac{T_2}{T_1}\right)^{c_V} = \left(\frac{V_2}{V_1}\right)^R \Rightarrow \left(\frac{T_2}{T_1}\right)^{\frac{R}{c_V}} = \left(\frac{V_2}{V_1}\right)^{\frac{R}{c_V}} \Rightarrow \left(\frac{T_2}{T_1}\right)^{\gamma} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$$\text{thus: } \frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1} \Rightarrow \left(\frac{T_2}{T_1}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma}{\gamma-1}} \Rightarrow P_2 V_2^{\gamma} = P_1 V_1^{\gamma} = PV^{\gamma} = \text{const}$$

Isothermal Reversible Expansion $w = q = RT \ln \left(\frac{V_2}{V_1}\right) = RT \ln \left(\frac{P_1}{P_2}\right)$

An isothermal process is one of constant internal energy during which the work done by the system equals the thermal energy absorbed by the system

A decrease in pressure results in the work done by the reversible isothermal process (area under curve) exceeds that done by the reversible adiabatic process. This difference is from the isothermal process block thermal energy into system.

Other diagram shows 3 process paths for a fixed quality of gas from state 1 to state 2

$$\delta w = PdV \text{ and } w = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} \frac{RT}{V} dV = RT \ln(2) \text{ valid in isothermal expansion}$$

The transfer of thermal energy (q) and the performance of work (w) are processes which occur on the system and are not intrinsic to the system and are not properties of the system. When performed on or by the system they do however change the properties of the system. In the case of a cyclic process the change in U is zero

In the reversible adiabatic expansion, where $(U_2 - U_1) = -w$, the process since the process is adiabatic ($q=0$), thus the path of the process was specified and AU could be calculated

U' is an extensive state variable, a simple system consisting of a given amount of substance of fixed composition, the value of U' is fixed once any two independent variables are fixed. If temperature and volume are chosen, then:

$$U' = U'(V', T) \text{ and } dU' = \left(\frac{\partial U'}{\partial T}\right)_{V'} dT + \left(\frac{\partial U'}{\partial V'}\right)_{T'} dV' \text{ DeHoff calls } \left(\frac{\partial U'}{\partial T}\right)_{V'} \& \left(\frac{\partial U'}{\partial V'}\right)_{T'} \text{ coefficient relations}$$

$$dU' = \delta q - \delta w; \delta q = C_V dT \& \delta w = -PdV'; dU' = C_V dT + PdV'; \text{ thus } \left(\frac{\partial U'}{\partial V'}\right)_T = P$$

Reversible Isothermal Expansion with Entropy (q/T)

$$w_{rev} = \int_{V_A}^{V_B} PdV = \int_{V_A}^{V_B} \frac{RT}{V} dV = RT \ln \left(\frac{V_B}{V_A}\right) = q_{rev}$$

(+) w since work done by system; (+) q since thermal energy into the system

$$\Delta S'_{gas} = S'_B - S'_A = \frac{q_{rev}}{T} = \frac{w_{rev}}{T} = R \ln \left(\frac{V_B}{V_A}\right); \text{ The entropy of the gas increases}$$

$$\Delta S'_{heat reservoir} = \frac{-q}{T} = -\Delta S'_{gas} = R \ln \left(\frac{V_A}{V_B}\right) < 0$$

$$\Delta S'_{gas} + \Delta S'_{heat reservoir} = R \ln \left(\frac{V_B}{V_A}\right) + R \ln \left(\frac{V_A}{V_B}\right) = 0$$

Entropy (S) - A state variable and its change during process is a measure of its irreversibility

$A \rightarrow B$ reversibly: $\Delta S(gas) = \Delta S'_{A \rightarrow B}$; $A \rightarrow B$ reversibly: $\Delta S(gas) = \Delta S'_{A \rightarrow B}$

The same change in entropy (state function) for gas: $\Delta S(gas) = \Delta S'_{irrev} = \Delta S'_{rev}$

Since the increase in entropy of the gas is not compensated by a decrease in entropy of the surroundings, the entropy of the universe increases during this irreversible process and it is in the gas

Isothermal reversible expansion: $\Delta U = q_{rev} - w_{rev} = 0$; $q_{rev} = w_{rev} = RT \ln \left(\frac{V_B}{V_A}\right)$

Free expansion: $\Delta U = q_{irrev} - w_{irrev} = 0$; $q_{irrev} = w_{irrev} = 0$; $q_{rev} = w_{rev} = 0$

Maximum work is done during the reversible process, no work (minimum work) is done during the free expansion

$$\begin{aligned} dG &= -SdT + VdP \\ dU &= TdS - PdV \\ dH &= TdS + VdP \\ dA &= -PdV - SdT \end{aligned}$$

$$G \equiv H - TS \quad \text{free enthalpy}$$

$$G = U + PV - TS$$

$$dG = dU + PdV + VdP - TdS - SdT$$

$$dG = -SdT + VdP$$

$$T = \left(\frac{\partial H}{\partial S}\right)_P = \left(\frac{\partial U}{\partial S}\right)_P \quad S = -\left(\frac{\partial A}{\partial T}\right)_P = -\left(\frac{\partial G}{\partial T}\right)_P$$

$$V = \left(\frac{\partial H}{\partial P}\right)_S \quad V = \left(\frac{\partial G}{\partial P}\right)_T$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_S \quad P = -\left(\frac{\partial A}{\partial V}\right)_T$$

$$\begin{aligned} U' &= U'(S', V') \\ H' &= H'(S', P) \\ A' &= A'(T, V') \\ G' &= G'(T, P) \end{aligned}$$

For simple closed systems, these are the four possible relationships leading to the four fundamental equations.

$$\begin{aligned} dU &= TdS - PdV \\ dH &= TdS + VdP \\ dA &= -SdT - PdV \\ dG &= -SdT + VdP \end{aligned}$$

Now suppose the first law is written to include another form of work which may be performed on or by the system, magnetic work

$$\delta w_{mag} = -V' \mu_0 \mathcal{H} \cdot d\mathcal{M} = -V' \mu_0 \mathcal{H} \cdot dM$$

where V' is the volume and we assume $\mathcal{H} // M$

$$\begin{aligned} dU_{mag} &= TdS - PdV + V_{mol} \mu_0 \mathcal{H} dM \\ dH_{mag} &= TdS + VdP - V_{mol} \mu_0 M d\mathcal{H} \\ dA_{mag} &= -SdT - PdV + V_{mol} \mu_0 \mathcal{H} dM \\ dG_{mag} &= -SdT + VdP - V_{mol} \mu_0 M d\mathcal{H} \end{aligned}$$

The Chemical Potential

$$G' = G(T, P, n_1, n_2, n_3, \dots)$$
$$dG' = \left(\frac{\partial G'}{\partial T}\right)_{P, n_i} dT + \left(\frac{\partial G'}{\partial P}\right)_{T, n_i} dP + \sum_i \left(\frac{\partial G'}{\partial n_i}\right)_{T, P, n_j} dn_i$$
$$dG' = \left(\frac{\partial G'}{\partial T}\right)_{P, n_i} dT + \left(\frac{\partial G'}{\partial P}\right)_{T, n_i} dP + \sum_i \left(\frac{\partial G'}{\partial n_i}\right)_{T, P, n_j} dn_i$$

$\left(\frac{\partial G'}{\partial n_i}\right)_{T, P, n_j}$ is called the chemical potential of species i , and is usually denoted as μ_i .

The Chemical Potential

$$dU' = TdS' - PdV' + \sum \mu_i dn_i \quad U' = U'(S', V', n_i)$$
$$dH' = TdS' + V'dP + \sum \mu_i dn_i \quad H' = H'(S', P, n_i)$$
$$dA' = -SdT - PdV' + \sum \mu_i dn_i \quad A' = A'(T, V', n_i)$$
$$dG' = -SdT + V'dP + \sum \mu_i dn_i \quad G' = G'(T, P, n_i)$$

Thermodynamic Relations

The Coefficient Relations

Start with the Molar Fundamental Equations

$$\begin{aligned} dU_{mag} &= TdS - PdV + V_{mol} \mu_0 \mathcal{H} dM \\ dH_{mag} &= TdS + VdP - V_{mol} \mu_0 M d\mathcal{H} \\ dA_{mag} &= -SdT - PdV + V_{mol} \mu_0 \mathcal{H} dM \\ dG_{mag} &= -SdT + VdP - V_{mol} \mu_0 M d\mathcal{H} \end{aligned}$$

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}$$
$$\left(\frac{\partial^2 S}{\partial U^2}\right)_V = -\frac{1}{T^2} \frac{\partial T}{\partial U} < 0$$

$$\begin{aligned} dU_{mag} &= TdS - PdV + V_{mol} \mu_0 \mathcal{H} dM \\ dH_{mag} &= TdS + VdP + V_{mol} \mu_0 M d\mathcal{H} \\ dG_{mag} &= -SdT + VdP + V_{mol} \mu_0 M d\mathcal{H} \end{aligned}$$

OR

$$\begin{aligned} dU_{mag} &= TdS - PdV - V_{mol} \mu_0 M d\mathcal{H} \\ dH_{mag} &= TdS + VdP - V_{mol} \mu_0 M d\mathcal{H} \\ dA_{mag} &= -SdT - PdV - V_{mol} \mu_0 M d\mathcal{H} \\ dG_{mag} &= -SdT + VdP - V_{mol} \mu_0 M d\mathcal{H} \end{aligned}$$

The Chemical Potential and the Energy Functions

$G = G(T, P)$ for molar values of G
 $G' = G(T, P, n_i)$ for total values of G'
 $G' = nG$

Multi - Component Systems
 $G' = G(T, P, n_1, n_2, n_3, \dots)$

$$dG' = \left(\frac{\partial G'}{\partial T}\right)_{P, n_i} dT + \left(\frac{\partial G'}{\partial P}\right)_{T, n_i} dP + \sum_i \left(\frac{\partial G'}{\partial n_i}\right)_{T, P, n_j} dn_i$$

+ $\left(\frac{\partial G'}{\partial n_i}\right)_{T, P, n_j} dn_i$ etc.

The Chemical Potential and U, H, A and G

$$dU' = TdS' - PdV' + \sum_i \left(\frac{\partial U'}{\partial n_i}\right)_{T, P, n_j} dn_i$$
$$dH' = TdS' + V'dP + \sum_i \left(\frac{\partial H'}{\partial n_i}\right)_{T, P, n_j} dn_i$$
$$dA' = -SdT - PdV' + \sum_i \left(\frac{\partial A'}{\partial n_i}\right)_{T, V, n_j} dn_i$$
$$dG' = -SdT + V'dP + \sum_i \left(\frac{\partial G'}{\partial n_i}\right)_{T, P, n_j} dn_i$$
$$\mu_i = \left(\frac{\partial G'}{\partial n_i}\right)_{T, P, n_j} = \left(\frac{\partial U'}{\partial n_i}\right)_{T, P, n_j} = \left(\frac{\partial H'}{\partial n_i}\right)_{T, P, n_j} = \left(\frac{\partial A'}{\partial n_i}\right)_{T, P, n_j}$$

Helmholtz Free Energy: Application Vapor and Solid Equilibrium

Schematic of a crystalline solid and its vapor with pressure below its triple point at three different temperatures.
(a) $T = 0$ K; (b) $0 < T$; (c) T very large. The volume of the system is fixed.

$$A' = A'(T, V, n_i)$$

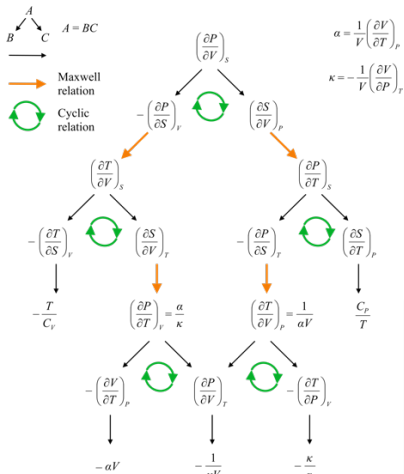
$$\begin{aligned} dU_{mag} &= TdS - PdV + V_{mol} \mu_0 \mathcal{H} dM \\ dH_{mag} &= TdS + VdP - V_{mol} \mu_0 M d\mathcal{H} \\ dA_{mag} &= -SdT - PdV + V_{mol} \mu_0 \mathcal{H} dM \\ dG_{mag} &= -SdT + VdP - V_{mol} \mu_0 M d\mathcal{H} \end{aligned}$$

The Coefficient Relations Intensive Variables

$$T = \left(\frac{\partial U}{\partial S}\right)_{V, M} = \left(\frac{\partial H}{\partial S}\right)_{P, M}$$
$$P = -\left(\frac{\partial U}{\partial V}\right)_{S, M} = -\left(\frac{\partial A}{\partial V}\right)_{T, M}$$
$$\mathcal{H} = \frac{1}{V} \left(\frac{\partial U}{\partial M}\right)_{S, V} = \frac{1}{V} \left(\frac{\partial A}{\partial M}\right)_{T, V}$$

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \quad \left(\frac{\partial^2 S}{\partial U^2}\right)_V = -\frac{1}{T^2} \frac{\partial T}{\partial U} < 0$$

What happens as $T \rightarrow 0$?
Infinite slope and minimum in U and zero in SU



The Maxwell Relations for a One Component Open System

$$dU' = TdS' - PdV' + \mu dn$$

$$\left(\frac{\partial T}{\partial V'} \right)_{S',n} = - \left(\frac{\partial P}{\partial S'} \right)_{T',n}$$

$$\left(\frac{\partial T}{\partial n} \right)_{S',V'} = \left(\frac{\partial \mu}{\partial S'} \right)_{T',V'}$$

$$\left(\frac{\partial P}{\partial n} \right)_{T',V'} = - \left(\frac{\partial \mu}{\partial V'} \right)_{S',T'}$$

The Maxwell Relations for a One Component Open System with Applied Magnetic Field

$$dU' = TdS' - PdV' + \mu dn + V' \mu_0 \mathcal{H} dM$$

$$\left(\frac{\partial T}{\partial V'} \right)_{S',M} = - \left(\frac{\partial P}{\partial S'} \right)_{T',M}$$

$$\left(\frac{\partial T}{\partial n} \right)_{S',M} = \left(\frac{\partial \mu}{\partial S'} \right)_{T',M}$$

$$\left(\frac{\partial P}{\partial n} \right)_{T',M} = - \left(\frac{\partial \mu}{\partial V'} \right)_{S',T'}$$

5. One mole of an ideal gas is taken on the path $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$ as shown below

(1) $A \rightarrow B$ is a reversible isothermal expansion of the gas;

(2) $B \rightarrow C$ is a reversible adiabatic expansion of the gas;

(3) $C \rightarrow D$ is a reversible isothermal compression of the gas;

(4) $D \rightarrow A$ is a reversible adiabatic compression of the gas.

From the initial state of a quantity of monatomic ideal gas is $P=1$ atm, $V=1$ liter, and $T=373$ K.

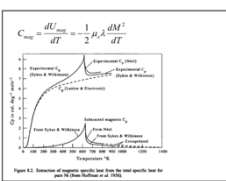
The gas is isothermally expanded to a volume of 2 liters and is then cooled at constant pressure to the volume V . This volume is such that a reversible adiabatic compression to a pressure of 1 atm returns the system to its initial state. All of the changes of state are conducted reversibly.

Calculate the value of V and the total work done on or by the gas.

2. The initial state of a quantity of monatomic ideal gas is $P=1$ atm, $V=1$ liter, and $T=373$ K.

The gas is isothermally expanded to a volume of 2 liters and is then cooled at constant pressure to the volume V . This volume is such that a reversible adiabatic compression to a pressure of 1 atm returns the system to its initial state. All of the changes of state are conducted reversibly.

Calculate the value of V and the total work done on or by the gas.



The Three TdS Equations

- $TdS = c_p dT + \frac{T\alpha}{\beta_T} dV$
- $TdS = c_p dT - TV\alpha dP$
- $TdS = c_p \frac{\beta_T}{\alpha} dP + \frac{c_p}{\alpha V} dV$

The Maxwell Relations for a One Component Open System

$$dU' = TdS' - PdV' + \mu dn$$

$$dH' = \dots$$

$$dA' = \dots$$

$$dG' = \dots$$

Total of 12 (4x3) Maxwell Relations for a one component open system

The Maxwell Relations for a One Component Open System with Applied Magnetic Field

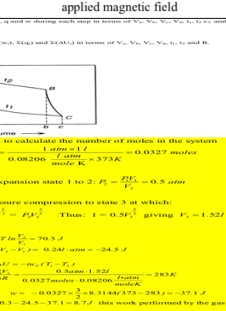
$$dU' = TdS' - PdV' + \mu dn + V' \mu_0 \mathcal{H} dM$$

$$dH' = \dots$$

$$dA' = \dots$$

$$dG' = \dots$$

Total of 24 (6x4) Maxwell Relations for open system with applied magnetic field



4a. Show that $\left(\frac{\partial T}{\partial P} \right)_H = -\frac{V(1-\alpha T)}{C_p}$ (Hint: see page 74 of Deffold)

b. Determine the value of $\left(\frac{\partial T}{\partial P} \right)_H$ for an ideal gas.

c. Show that the dimensions of the left hand side of the equations are the same as the right hand side

a. $dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP$

$dH = 0$

$\left(\frac{\partial T}{\partial P} \right)_H = - \left(\frac{\left(\frac{\partial H}{\partial P} \right)_T}{\left(\frac{\partial H}{\partial T} \right)_P} = - \frac{\left(\frac{\partial H}{\partial P} \right)_T}{C_p}$

But $\left(\frac{\partial H}{\partial P} \right)_T = V(1-\alpha T)$

$\left(\frac{\partial T}{\partial P} \right)_H = - \frac{V(1-\alpha T)}{C_p}$

b. For an ideal gas $\alpha = \frac{1}{T} : \left(\frac{\partial T}{\partial P} \right)_H = 0$

c. $\left(\frac{\partial T}{\partial P} \right)_H = \frac{\text{temperature}}{\text{pressure}} = \frac{\text{temperature}}{R \cdot \frac{\text{volume}}{\text{volume}}} = \frac{\text{volume}}{R}$

$\frac{V(1-\alpha T)}{C_p} = \frac{\text{volume}}{R}$

The slope of an isotherm is :

$$PV = RT$$

$$\left(\frac{\partial P}{\partial V} \right)_T = \frac{RT}{V^2} = \frac{PV}{V^2} = \frac{P}{V}$$

The slope of an adiabatic is :

$$PV^\gamma = \text{constant}$$

$$\left(\frac{\partial P}{\partial V} \right)_S = -\gamma \cdot \text{constant} \cdot V^{\gamma-1} = -\gamma \frac{P}{V}$$

The ratio for same P and V is given as:

$$\frac{-\gamma \frac{P}{V}}{-\frac{P}{V}} = \gamma > 1$$

2. a. Calculate the work performed by the Carnot cycle shown in the figure below. The cycle is shown in the T-S diagram and the figure below shows the Carnot cycle using the T-S diagram.

b. What are the SI units for the area in the T-S diagram? Show that the dimensions match.

1a. Show that the following equation is valid:

$$\left(\frac{\partial A}{\partial V} \right)_T = -P - \frac{1}{\alpha T}$$

1b. Do the dimensions match? $S \cdot \frac{1}{\alpha T} = \text{pressure?}$

2. a. Start with the equation from MATSIS (Lecture 1): $N = N(X, T, Z)$. X & Y are the independent variables.

$\left(\frac{\partial N}{\partial X} \right)_T = \left(\frac{\partial N}{\partial T} \right)_X$

$\left(\frac{\partial N}{\partial Z} \right)_T = \left(\frac{\partial N}{\partial T} \right)_Z$

$dA = -PdV - SdT$

$\left(\frac{\partial A}{\partial V} \right)_T = -P - \frac{S}{\alpha T}$

b. yes

$\frac{S}{T} = \frac{\text{entropy}}{T} = \text{pressure}$

3. Plot the energy functions *versus* the denoted variables. See example of U vs. V in Lecture 02. Be sure to have the correct slope and curvature for each plot.

4. The cycle shown below consists of two adiabatics (BC and DA) and two isotherms (AB and CD). Use the TdS equations to draw the T-S diagram for this cycle.

a. Explain what equation you used to draw the curves AB, BC, CD and DA in the TS diagram and be sure to indicate your logic.

b. What are the respective signs of the areas enclosed by the PV and TS curves?

TS diagram and PV diagram for a Carnot cycle.

a. Explain what equation you used to draw the curves AB, BC, CD and DA in the TS diagram and be sure to indicate your logic.

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TS diagram and PV diagram for a Carnot cycle.

a. Explain what equation you used to draw the curves AB, BC, CD and DA in the TS diagram and be sure to indicate your logic.

b. What are the respective signs of the areas enclosed by the PV and TS curves?

6. Show that: $\frac{\beta_T}{\beta_S} = \frac{c_p}{c_v} = \gamma$ where $\beta_T \equiv \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$ and $\beta_S \equiv \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S$

Solution

Start with the First and Second Law

1. $TdS = c_p dT + \frac{T\alpha}{\beta_T} dV$

2. $TdS = c_v dT - TV\alpha dP$

Set $S = 0$ and divide 2 by 1

1. $c_p dT = -\frac{T\alpha}{\beta_T} dV$

2. $c_v dT = TV\alpha dP$

$\frac{c_p}{c_v} = -\frac{TV\alpha}{T\alpha} \left(\frac{dP}{dV} \right)_S = (V\beta_T) \frac{1}{(V\beta_S)} = \frac{\beta_T}{\beta_S}$

Other kinds of caloric effects?

$dS = \left(\frac{\partial S}{\partial T} \right)_{P,\mathcal{H}} dT + \left(\frac{\partial S}{\partial P} \right)_{T,\mathcal{H}} dP + \left(\frac{\partial S}{\partial \mathcal{H}} \right)_{T,P} d\mathcal{H}$

Heat capacity c_p **piezocaloric** **magnetocaloric**

$dV = \left(\frac{\partial V}{\partial T} \right)_{P,\mathcal{H}} dT + \left(\frac{\partial V}{\partial P} \right)_{T,\mathcal{H}} dP + \left(\frac{\partial V}{\partial \mathcal{H}} \right)_{T,P} d\mathcal{H}$

Thermal expansion α **isothermal compressibility** **piezomagnetism**

$dM = \left(\frac{\partial M}{\partial T} \right)_{P,\mathcal{H}} dT + \left(\frac{\partial M}{\partial P} \right)_{T,\mathcal{H}} dP + \left(\frac{\partial M}{\partial \mathcal{H}} \right)_{T,P} d\mathcal{H}$

pyromagnetism **piezomagnetism** **susceptibility**

THE COMBINED STATEMENT OF THE FIRST AND SECOND LAWS OF THERMODYNAMICS

$dU' = TdS' - PdV' + \mu dn$

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$dU' = TdS' - PdV' + \mu dn + V' \mu_0 \mathcal{H} dM$

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Does Thermal energy Always Flow down a Temperature Gradient? (i)

Assume energy is transferred as q from T_C to T_H . (C for cold and H for hot)

$\Delta S_H = \frac{q}{T_H}$ $\Delta S_C = -\frac{q}{T_C}$

$\Delta S_T = \Delta S_H + \Delta S_C = \frac{q}{T_H} - \frac{q}{T_C}$

$\Delta S_T = q \left(\frac{1}{T_H} - \frac{1}{T_C} \right) < 0$

Does Thermal energy Always Flow down a Temperature Gradient? (ii)

When we assumed that thermal energy went from the cold system to the hot we found

$\Delta S_T = q \left(\frac{1}{T_H} - \frac{1}{T_C} \right) < 0$

This is contrary to the Second Law!

Thus heat can not flow spontaneously from a cold source to a hot source if the second law is correct!

U₂

U₁

The system is 1

The surroundings is 2

Assume system is closed (no Ac)

Constant Volume $dV = 0$

Now suppose energy leaves the system in the form of thermal energy and goes into the surroundings.

$\Delta U_1 < 0$

$\Delta S_{tot} = \Delta S_1 + \Delta S_2 = \Delta S_1 + \frac{\Delta U_1}{T} = \Delta S_1 - \frac{\Delta U_1}{T}$

Assume $S' = S(P, \mathcal{H}, T)$

$dS' = \left(\frac{\partial S'}{\partial P} \right)_{\mathcal{H},T} dP + \left(\frac{\partial S'}{\partial \mathcal{H}} \right)_{P,T} d\mathcal{H} + \left(\frac{\partial S'}{\partial T} \right)_{P,\mathcal{H}} dT$

Maxwell Relations:

$\left(\frac{\partial S'}{\partial P} \right)_{\mathcal{H},T} = - \left(\frac{\partial V}{\partial T} \right)_{P,\mathcal{H}}$ $\left(\frac{\partial S'}{\partial \mathcal{H}} \right)_{P,T} = V \mu_0 \left(\frac{\partial M}{\partial T} \right)_{P,\mathcal{H}}$

$dG' = -S' dT + V dP - M' d\mathcal{H}$

U₂

U₁

For this process to occur spontaneously,

$\Delta S_{tot} = \Delta S_1 + \frac{\Delta U_1}{T} > 0$

$\Delta U_1 - T \Delta S_1 < 0$

This equation includes changes in **system** only; it must be **negative**. We therefore define a state function, A as:

$\Delta A = \Delta U_1 - T \Delta S_1 < 0$

We call this the work function or the **Helmholtz Free Energy**

$dS' = - \left(\frac{\partial V}{\partial T} \right)_{P,\mathcal{H}} dP + V \mu_0 \left(\frac{\partial M}{\partial T} \right)_{P,\mathcal{H}} d\mathcal{H} + \frac{C_{\mathcal{H},P}}{T} dT$

$dS' = -\alpha V dP + V \mu_0 \left(\frac{\partial M}{\partial T} \right)_{P,\mathcal{H}} d\mathcal{H} + \frac{C_{\mathcal{H},P}}{T} dT$

$dS' = -\alpha V dP + V \mu_0 \left(\frac{\partial M}{\partial T} \right)_{P,\mathcal{H}} d\mathcal{H} + \frac{C_{\mathcal{H},P}}{T} dT = 0$ (adiabatic)

Thus, for constant P,

$dT = - \frac{V \mu_0 T}{C_{\mathcal{H},P}} \left(\frac{\partial M}{\partial T} \right)_{P,\mathcal{H}} d\mathcal{H}$