

Maxwell Relations

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$$G = Vdp - SdT + udn$$

$$\frac{\partial}{\partial x} \left( \frac{\partial f}{\partial y} \right) = \frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right)$$

# Thermodynamics

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## Unit 5: Pure Substance

### Lecture 29: The Tds equations and Energy equations

## Unit 5: Pure Substance

- Enthalpy
- The Helmholtz functions
- Gibbs functions
- Maxwell's Equations
- The Tds equations**
- Energy equations**
- Heat-capacity equations

$$v = \text{const}$$

$$T \left. \frac{\partial s}{\partial T} \right|_v = c_v$$

$$T ds = c_v dT + T \left. \frac{\partial s}{\partial T} \right|_v dT$$

$$\left. \frac{\partial s}{\partial T} \right|_v = \left. \frac{\partial p}{\partial T} \right|_v$$

$$T ds = c_v dT + T \left. \frac{\partial p}{\partial T} \right|_v dv$$

$$S = S(T, P)$$

## The first $TdS$ Equation

The entropy of a pure substance can be imagined as a function of  $T$  and  $V$ , i.e.  $S = f(T, V)$

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

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

$TdS = dQ$  for a reversible process, then

$$T \left(\frac{\partial S}{\partial T}\right)_V = C_v$$

And, from Maxwell's third equation,

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

$$TdS = C_v dT + T \left(\frac{\partial P}{\partial T}\right)_V dV$$

**The first  $Tds$  equation**

## Example 1

1 mole of a **van der Waals gas** undergoes a reversible **isothermal expansion** from a volume  $V_i$  to a volume  $V_f$ . How much heat has been transferred?

For 1 mole

$$TdS = C_v dT + T \left(\frac{\partial P}{\partial T}\right)_V dV$$

Using molar van der Waals equation of state.

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

$$TdS = C_v dT + RT \frac{dV}{V-b}$$

Since  $T$  is constant,  $C_v dT = 0$ ; and since the process is reversible,  $Q = \int TdS$ , Therefore,

$$Q = RT \int_{V_i}^{V_f} \frac{dV}{V-b}$$

$$Q = RT \ln \frac{V_f - b}{V_i - b}$$

## The Second $TdS$ Equation

The entropy of a pure substance can be imagined as a function of  $T$  and  $V$ , i.e.  $S = f(T, P)$

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

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

$$T \left(\frac{\partial S}{\partial T}\right)_P = C_p$$

And, from Maxwell's fourth equation,

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

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T}\right)_P dP \quad \text{The second } Tds \text{ equation}$$

### Case 1: Reversible isothermal change of pressure

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$TdS = -T \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$Q = -T \int \left(\frac{\partial V}{\partial T}\right)_P dP \quad \text{But} \quad \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad \Rightarrow \quad V\beta = \left(\frac{\partial V}{\partial T}\right)_P$$

$$Q = -T \int V\beta dP$$

which can be integrated when the dependence of  $V$  and  $\beta$  on the pressure is known. In the case of a solid or liquid, **neither  $V$  nor  $\beta$  is very sensitive to a change in pressure.**

**For example**, in the case of mercury, as the pressure is increased from zero to 1000 atm at  $0^\circ\text{C}$  the volume of 1 mole of mercury changed 0.3%, and  $\beta$  changed by 4%.

Therefore the volume and expansivity of solid and liquid assumed to be constant.

$$Q = -T \int V \beta dP$$

$$Q = -TV\beta \int_{P_i}^{P_f} dP$$

$$Q = -TV\beta(P_f - P_i)$$

It is seen from this result that, as the pressure is increased isothermally, heat will flow out if  $\beta$  is positive but, for a substance with a negative expansivity (such as water between 0 and 4°C), an isothermal increase of pressure causes an absorption of heat.

If the pressure on  $2 \times 10^{-5} \text{ m}^3$  of mercury at 0°C is increased reversibly and isothermally from zero to 1000 atm, the heat transferred will be

$$Q = -TV\beta P_f$$

Where  $T = 293\text{K}$ ,  $V = 2 \times 10^{-5} \text{ m}^3$ ,  $\beta = 1.81 \times 10^{-4} \text{ K}^{-1}$ ,  $P_f = 1.01 \times 10^8 \text{ Pa}$

$$Q = -(293) \times (2 \times 10^{-5})(1.81 \times 10^{-4})(1.01 \times 10^8) = -80.3 \text{ J}$$

i.e. 80.1 J of heat leaves the system in order to keep the temperature constant as the pressure increased.

## Case 2: Reversible adiabatic change of pressure

Then the entropy is constant in this process

$$TdS = 0 = C_p dT - T \left( \frac{\partial V}{\partial T} \right)_P dP$$

$$dT = \frac{T}{C_p} \left( \frac{\partial V}{\partial T} \right)_P dP \quad \text{But} \quad \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

$$dT = \frac{TV\beta}{C_p} dP$$

In the case of a solid or liquid, an increase of pressure of as much as 1000 atm produces only a small temperature change.

Also, experiment shows that  $C_p$  hardly changes even for an increase of 10,000 atm. The above equation, when applied to a solid or a liquid, may therefore be written

$$\Delta T = \frac{TV\beta}{C_p} (P_f - P_i)$$

$$\Delta T = \frac{TV\beta}{C_p}(P_f - P_i)$$

It is clear from the above that an adiabatic **increase of pressure** will produce an **increase of temperature** in any substance with a positive expansivity and a **decrease in temperature** in a substance with a negative expansivity.

### Example

If the pressure on 15 cm<sup>3</sup> of mercury ( $C_p=139$  J/kg.K and specific volume  $V=7.38 \times 10^{-5}$  m<sup>3</sup>/kg) at 20°C is increased at constant entropy from zero to 1000 atm, the temperature change will be

$$\Delta T = \frac{TV\beta}{C_p}P_f$$

$$\Delta T = \frac{(293)(7.38 \times 10^{-5})(1.81 \times 10^{-4})}{139}(1.01 \times 10^8) = 2.84K$$

# Energy Equation

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## The first Energy Equation the dependence of volume

If a pure substance undergoes an infinitesimal reversible process between two equilibrium states, the change of internal energy is

$$dU = TdS - PdV$$

Dividing by  $dV$ , we get

$$\frac{dU}{dV} = T \frac{dS}{dV} - P$$

where  $U$ ,  $S$ , and  $P$  are regarded as functions of  $T$  and  $V$ . If  $T$  is held constant, then the derivatives become partial derivatives, and

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

Using Maxwell's third equation,  $(\partial S/\partial V)_T = (\partial P/\partial T)_V$ , we get

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad \text{the first energy equation}$$

### Case 1: Ideal gas

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

$$P = \frac{nRT}{V}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{nR}{V} - P = 0$$

Therefore,  $U$  does not depend on  $V$ , but is a function of  $T$  only in an ideal gas

## Case 2: Van der Wools gas $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{R}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2} \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$

$$dU = C_V dT + \frac{a}{V^2} dV \Rightarrow U = \int (C_V dT) - \frac{a}{V} + \text{constant}$$

The internal energy of a van der Waals gas increases as the volume increases, with the temperature remaining constant.

## The second Energy Equation the dependence of pressure

$$dU = TdS - PdV$$

divide by  $dP$

$$\frac{dU}{dP} = T \frac{dS}{dP} - P \frac{dV}{dP}$$

where  $U$ ,  $S$ , and  $V$  are imagined to be functions of  $T$  and  $P$ . If  $T$  is held constant, then the derivatives become partial derivatives, and

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

Using Maxwell's fourth equation,  $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ , we get

$$\left(\frac{\partial U}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial P}\right)_T \quad \text{the second energy equation}$$

## Problem to solve by yourself

Derive the third  $TdS$  Equation

$$T dS = C_V \left( \frac{\partial T}{\partial P} \right)_V dP + C_P \left( \frac{\partial T}{\partial V} \right)_P dV$$

and show that the three  $TdS$  equations may be written as follows

$$\begin{aligned} (a) \quad T dS &= C_V dT + \frac{\beta T}{\kappa} dV. \\ (b) \quad T dS &= C_P dT - V\beta T dP. \\ (c) \quad T dS &= \frac{C_V \kappa}{\beta} dP + \frac{C_P}{\beta V} dV. \end{aligned}$$

إلى اللقاء مع المحاضرة (٣٠)

**Heat-capacity equations**