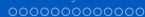
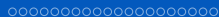


Thermodynamics in VC210

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Outline

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First law of thermodynamics

$$U = Q + W \quad (1)$$

Remarks:

- Differential form & $U = f(T)$
- W - work, including expansion work and non-expansion work. However, we only discuss the expansion work here.

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- Relationship with Kinetic Molecular Theory (KMT).

KMT & Heat capacity¹

	Atoms	Linear molecules	Nonlinear molecules
$C_{V,m}$	$\frac{3}{2}R$	$\frac{5}{2}R$	$3R$
$C_{P,m}$	$\frac{5}{2}R$	$\frac{7}{2}R$	$4R$

Figure: $C_{V,m}$ and $C_{P,m}$ of three types of molecules.

¹You may refer to *Chemicle Principle* pp. 402

The second law of thermodynamics

Clausius Statement

Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time.

The second law of thermodynamics

Kelvin Statement

It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature.

It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.

Entropy

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- Calculation of entropy.

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- Gibbs's free energy criterion.
- Calculation of Gibbs's free energy.

The third law of thermodynamics

$$S \rightarrow c \quad \text{as} \quad T \rightarrow 0 \text{ K}$$

Especially, $c = 0$ when the object is **perfect crystal**.

The zeroth law of thermodynamics

content

If two thermodynamic systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.

Practical Formula

$$Q_V = \Delta U \quad (6)$$

$$Q_p = \Delta H \quad (7)$$

$$C_V = \frac{\Delta U}{\Delta T} \quad (8)$$

$$C_p = \frac{\Delta H}{\Delta T} \quad (9)$$

$$\Delta S_{\text{surrounding}} = -\frac{\Delta H}{T} \quad (10)$$

$$S = k \ln W \quad (11)$$

Practical Formula

phase change

$$\Delta S = \frac{Q_R}{T} \quad (12)$$

physical change with constant pressure

$$\Delta S = nC_{V,m} \ln \left(\frac{T_2}{T_1} \right) + nR \ln \left(\frac{V_2}{V_1} \right) \quad (13)$$

physical change with constant volume

$$\Delta S = nC_{p,m} \ln \left(\frac{T_2}{T_1} \right) + nR \ln \left(\frac{p_1}{p_2} \right) \quad (14)$$

Practical Formula

Clausius–Clapeyron relation

$$\ln \left(\frac{p_2}{p_1} \right) = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (15)$$

constant temperature

$$\Delta G = \int V dp \quad \text{since} \quad dG = -s dT + V dp \quad (16)$$

Outline

Bohn-Haber Cycle

The standard molar enthalpy of combustion of ethanol ($\text{C}_2\text{H}_5\text{OH}$) and acetic acid (CH_3COOH) is -136.50 and -67.50 kJ/mol.

The enthalpy of dissolution is 11.71 and 1.46 kJ/mol correspondingly. Calculate the enthalpy of oxidation of ethanol in water solution.

Liquid-Solution

Liquid A and B form an ideal solution. The solution containing 1 mol A and 2 mol B at 343.2 K has a vapor pressure of 50.663 kPa.

If 3 mol A is added, the vapor pressure of the solution increases to 70.928 kPa. Calculate (1) p_A^* and p_B^* at 343.2 K; (2) the gaseous composition of the first mixed solution.