

ADVANCED THERMODYNAMICS

1st Law of Thermodynamics

Even though energy can take different forms, but the total amount of the energy of the system and the energy of the surroundings is constant.

For a closed system: $\Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0$

We know from the first law: $\Delta E_{\text{system}} = \Delta U$

Sign convention that we apply: $\Delta U = Q - W$ when the heat is going into the system from the environment is positive and vice versa, the work made by the system is positive and the work made on the system is negative.

Remember that U is an extensive quantity. Dividing by the mass we get an intensive quantity. Also remember that U is a status function, it only depends on the initial state and the final state of the system.

We can also use the enthalpy H: $\Delta H = Q - W_s$. This expression is used for open system but it's also valid for closed system. W_s is the work made by mechanical parts (the so called shaft work). Enthalpy is a status function too.

2nd Law of Thermodynamics

$$dS = \frac{\delta Q}{T} \quad \text{REVERSIBLE}$$

This equation says that it's not possible for a process to entirely convert heat into work with no other effect on system and surroundings.

If we consider a heat exchange, some of this heat is given to the environment!

Another consequence: the heat can only flows spontaneously from higher temperature level to lower temperature level (Lord Kelvin).

Phase equilibria

In the undergraduate thermodynamics course we use the concept of chemical potential μ in order to give a general expression for phase equilibria.

If we have more than one component in L-V system, we assume that at some point this system reach the equilibrium state. What are the general condition for phase equilibria?

$$\mu_{iL} = \mu_{iV}$$

The two phase have the same chemical potential.

This equation is very elegant but not practical.

1

We need to introduce a new quantity called fugacity. The definition of fugacity comes from this equation :

$$d\mu_i = RT d \ln f_i \quad \text{at const } T$$

In order to complete our definition we specify that :

$$\lim_{P \rightarrow 0} \frac{f_i}{P_i} = 1$$

When pressure goes to zero the fugacity goes to the same value of the pressure (partial pressure).

Fugacity is still related to the partial pressure by a fugacity coefficient ϕ_i . (ideal case : $\phi_i = 1$) (there are tables for ϕ_i)

$$f_i = \phi_i P_i$$

So the fugacity coefficient is function of : reduced temperature T_r (T/T_c , where the critical temperature can be calculated by summing all the critical temperature of each component times the molar fraction of each component). Remember that the temperature is the same for every component under equilibrium.

The equation that describe phase equilibria can be write in terms of fugacity :

$$f_{iL} = f_{iV}$$

The reason why is that we have a simple relation between fugacity and molar fraction for an ideal system.

$$f_{iV} = f_{iV}^0 y_i$$

$f_{iV}^0 y_i$ is the product of the fugacity of the same species under standard condition (when the component is pure, so there are no other component in our system)(same T and P of the mixture) and the molar fraction of the component in our mixture.

For the liquid phase : $f_{iL} = f_{iL}^0 x_i$

For an ideal gas when pressure goes to zero the fugacity is a partial pressure :

$$f_{iV} = P_i = P y_i$$

The fugacity in standard condition becomes the total pressure.

We can say that the fugacity is proportional to the molar fraction thanks to the assumption that there are no interaction between particles in our system. In liquid state this assumption doesn't work, so we have to assume that molecular interaction between different species are the same. (the interaction between A molecules with B molecules is the same of A-A or B-B)

So with this assumption we can extend this ideal approx. to the liquid state (through exponential Poynting factor derivation, we neglect the relation between fugacity and pressure of the liquid state).

Advanced Thermodynamics Guide

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Table of Contents Advanced Thermodynamics Guide

1. Understanding the eBook Advanced Thermodynamics Guide
 - The Rise of Digital Reading Advanced Thermodynamics Guide
 - Advantages of eBooks Over Traditional Books
2. Identifying Advanced Thermodynamics Guide
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Advanced Thermodynamics Guide
 - User-Friendly Interface
4. Exploring eBook Recommendations from Advanced Thermodynamics Guide
 - Personalized Recommendations
 - Advanced Thermodynamics Guide User Reviews and Ratings
 - Advanced Thermodynamics Guide and Bestseller Lists
5. Accessing Advanced Thermodynamics Guide Free and Paid eBooks
 - Advanced Thermodynamics Guide Public Domain eBooks
 - Advanced Thermodynamics Guide eBook Subscription Services
 - Advanced Thermodynamics Guide Budget-Friendly Options

6. Navigating Advanced Thermodynamics Guide eBook Formats
 - ePub, PDF, MOBI, and More
 - Advanced Thermodynamics Guide Compatibility with Devices
 - Advanced Thermodynamics Guide Enhanced eBook Features
7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Advanced Thermodynamics Guide
 - Highlighting and Note-Taking Advanced Thermodynamics Guide
 - Interactive Elements Advanced Thermodynamics Guide
8. Staying Engaged with Advanced Thermodynamics Guide
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Advanced Thermodynamics Guide
9. Balancing eBooks and Physical Books Advanced Thermodynamics Guide
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Advanced Thermodynamics Guide
10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
11. Cultivating a Reading Routine Advanced Thermodynamics Guide
 - Setting Reading Goals Advanced Thermodynamics Guide
 - Carving Out Dedicated Reading Time
12. Sourcing Reliable Information of Advanced Thermodynamics Guide
 - Fact-Checking eBook Content of Advanced Thermodynamics Guide
 - Distinguishing Credible Sources
13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
14. Embracing eBook Trends
 - Integration of Multimedia Elements

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