

# Notes of Ilya Prigogine's – *Modern Dynamics*

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# Part I

## Historical Roots

# Chapter 1

## The Basic Concepts

### 1.1 Thermodynamic Systems

- **Isolated systems** do not exchange energy or matter with the exterior.
- **Closed systems** exchange energy with the exterior but not matter.
- **Open systems** exchange both energy and matter with the exterior.

The **state** of a system is specified in terms of macroscopic **state variables** such as volume  $V$ , pressure  $p$ , temperature  $T$ , mole number of the chemical constituents  $N_k$ . The two laws of thermodynamics are founded on the concepts of energy  $U$ , and entropy  $S$ , which are **functions of state variables**. It is convenient to classify thermodynamic variables into two categories: variables such as volume and mole number, which are proportional to the size of the system, are called **extensive variables**. Variables such as temperature  $T$  and pressure  $p$ , that specify a local property, which are independent of the size of the system, are called **intensive variables**. If the temperature is not uniform, heat will flow until the entire system reaches a state of uniform temperature, the state of **thermal equilibrium**.

In the state of thermal equilibrium, the values of total internal energy  $U$  and entropy  $S$  are specified by

$$U = U(T, V, N_k), S = S(T, V, N_k) \quad (1.1)$$

The value of extensive variable can also be specified by other extensive variables:

$$U = U(S, V, N_k), S = S(U, V, N_k) \quad (1.2)$$

Intensive variables can be expressed as derivatives of one extensive variable with respect to another. For example,  $T = (\partial U / \partial S)_{V, N_k}$

### 1.2 Equilibrium and Nonequilibrium Systems

If a physical system is isolated, its state evolves *irreversibly* towards a time-invariant state in which we see no further physical or chemical change in the system. It is a state characterized

by a uniform temperature throughout the system. This is the state of **thermodynamic equilibrium**.

The evolution of a state of a state towards the state of equilibrium is due to irreversible process. At equilibrium, these processes vanish. Thus, a nonequilibrium state can be characterized as a state in which irreversible processes drive the system to the state of equilibrium.

If a system A is in equilibrium with system B and if B is in equilibrium with system C, then it follows that A is in equilibrium with C. This "transitivity" of the state of equilibrium is some times called the **zeroth law**. Thus, equilibrium systems have one uniform temperature and for these systems there exist state functions of energy and entropy. Uniformity of temperature, however, is not a requirement for the entropy or energy of a system to be well defined. For **nonequilibrium systems** in which the temperature is not uniform but is well defined locally, we can define density of thermodynamic quantities such as energy and entropy. Then the system's energy and entropy can be expressed as  $S = \int_V s(T(x), n_k(x))dV$ ,  $U = \int_V u(T(x), n_k(x))dV$ ,  $N = \int_V n_k(x)dV$ . So in nonuniform systems, the total energy U is no longer a functions of other extensive variables such as S, V and N.

## 1.3 Temperature, Heat and Quantitative Laws of Gases

**Definition 1.1.**  $1\text{Pa}=1\text{Nm}^{-2}$ ,  $1\text{bar}=10^5\text{Pa}$ ,  $(T/\text{K})=(T/^\circ\text{C}) + 273.15$

**Heat** was initially thought to be an indestructible substance called the **caloric**. However, in the 19th century it was established that heat was not an indestructible caloric but a form of energy that can convert to other forms. However, we still use **caloric** to measure heat.

A series of experiments setup up the **law of ideal gases**  $pV = NRT$ ,  $R = 8.31441\text{JK}^{-1}\text{mol}^{-1}$ . For a mixture of ideal gases we have the **Dalton law of partial pressures**, if  $p_k$  is the partial pressure due to component k, then  $p_k V = N_k RT$ . Since a gas expanding into vacuum does not do any work during the processes of expansion, its energy does not change. The fact that temperature does not change during this expansion into vacuum while the volume and pressure do change, implies that the energy of a given amount of ideal gas depends only on its temperature, not on volume or pressure. Thus the energy of the ideal gas can be written as  $U(T, N) = NU_m(T)$ , which  $U_m$  is the total internal energy per mole which can be expressed as  $U_m = cRT + U_0$ , where  $U_0$  is constant, for monatomic gases such as He and Ar,  $c=3/2$ , for diatomic gases such as  $N_2, O_2$ ,  $c=5/2$ . In the ideal gas equation, the volume of ideal gas can be compressed to infinite small. However, it is contradiction to physical intuition. In 1873, van der Waals proposed an equation in which he incorporated the effects of attractive forces between molecules and molecular size on the pressure and volume of gas.

$$(p + aN^2/V^2)(V - Nb) = NRT \quad (1.3)$$

## 1.4 States of Matter and the van der Waals Equation

In thermodynamics the various states of matter - solid, liquid, gas - are often referred to as **phases**. Joseph Black and James Watt discovered another interesting phenomenon associated with the changes of phase: at the melting or the boiling temperature, the heat supplied



to a system does not produce an increase in temperature; it only converts the substance from one phase to another. The van der Waals equation also exhibits a **critical temperature**  $T_c$ : if the temperature  $T$  is greater than  $T_c$  the p-V curve is always single-valued, indicating there is no transition to the liquid state. The van der Waals equation has two extrema for  $T < T_c$ . Below  $T_c$ , as  $T$  increases, these two extrema move closer and finally coalesce at  $T = T_c$ . Above the critical temperature there is no phase transition from a gas to a liquid. The pressure and volume at which this happens are called the **critical pressure**  $p_c$  and **critical volume**  $V_c$ . We note that if we regard  $p(v, T)$  as function of  $V$ , then at the critical point  $T = T_c, p = p_c, V = V_c$ . We have an inflection point, for the first and second derivatives vanish.

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0 \quad (1.4)$$

The solution is expressed as follows

$$T_c = \frac{8a}{27Rb} \quad p_c = \frac{a}{27b^2} \quad V_{mc} = 3b \quad (1.5)$$

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