General Physics I

Lect.22 State Variables

Based on Feynman Lectures Ch.44

Shengchao Li

lishengchao@westlake.edu.cn

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Thermo-dynamics

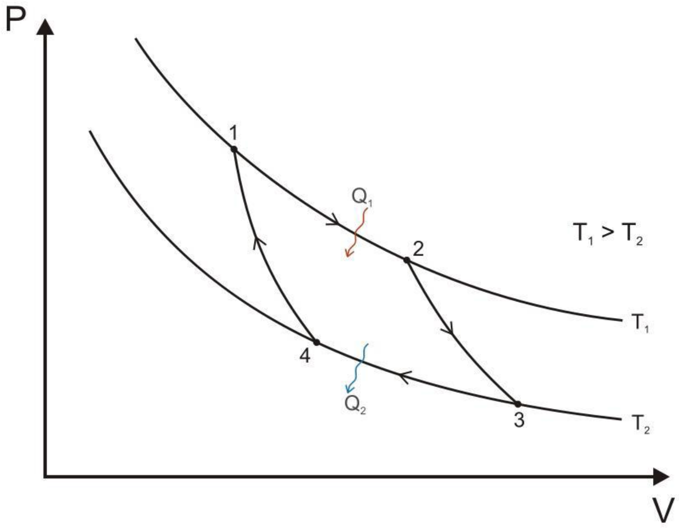
- Thermodynamics is the study of **heat** and **work**, how to use heat to do work.
- Thus, it is different than other study mechanics – they mostly talk about **actions 作用**
- In thermodynamics, we mostly talk about **energy 能量**

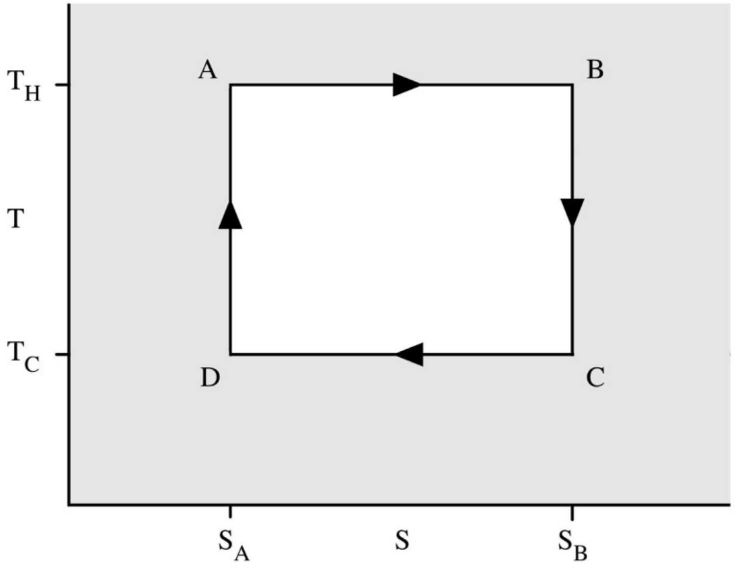
Conjugate sets of variables describing a system:

- Classical mechanics: (q, p) or (x,v); (E,t); (L,θ) … product in **action**
- Thermodynamics: (p, V); (T, S); (μ,N)… product in **energy**

A story of energy (potential) U and entropy S…this is what we shall discuss

Two sides of Carnot cycle





The behavior of a Carnot engine or refrigerator is best understood by using a temperature-entropy diagram (TS diagram), in which the thermodynamic state is specified by a point on a graph with entropy (S) as the horizontal axis and temperature (T) as the vertical axis.

Variables in thermodynamics

- The subject of thermodynamics is complicated because there are so many different ways of describing the **same thing — some energy**.

- **Ideal gas law** $PV=NkT$,

1. pressure depends on the temperature and on the volume $P(V,T)$
2. volume depends on the temperature and the pressure $V(T,P)$.

- For ***internal energy*** U, we can have $U(T,V)$, or $U(T,P)$, or $U(P,V)$.
- For ***entropy***, $S(T,V)$. And we can construct many other variables, such as: $F=U-TS$.
- For simplicity, we consider variables **T** and **V**, and their dependent functions **U** and **P**. Everything else should be a function of them.
- Since the variable of P depends on V and T, the **ordinary derivative** dP/dT is not enough. We define a new math symbol called **partial derivative**, $\partial P/\partial T$. This reminds us that P depends on V, as well as on T. To show that the other variable is held **constant**, we write the variable that is held constant as a subscript, $(\partial P/\partial T)_V$

Partial differentials

If a function rely on multiple variables, e.g., f(x,y), its partial differentials follows:

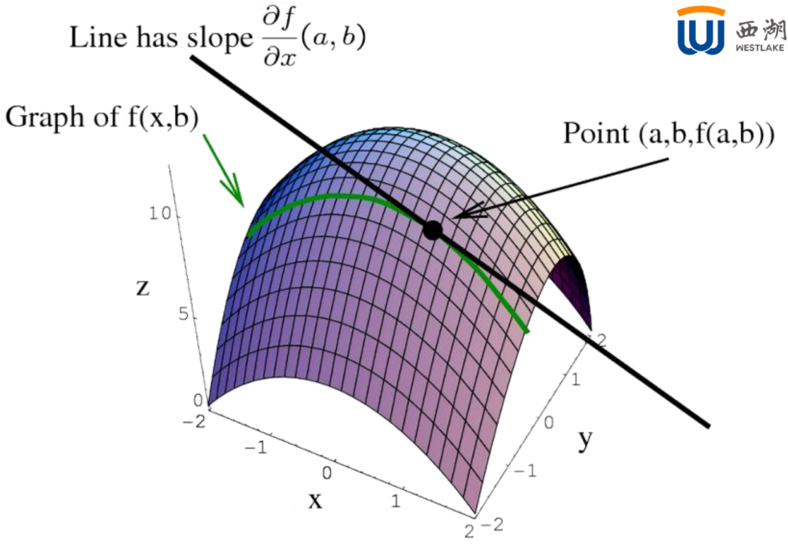
$$\left(\frac{\partial f}{\partial x}\right)_y = \lim_{\Delta x \to 0} \frac{f(x+\Delta x, y) - f(x,y)}{\Delta x}$$

$$\left(\frac{\partial f}{\partial y}\right)_x = \lim_{\Delta y \to 0} \frac{f(x, y+\Delta y) - f(x,y)}{\Delta y}$$

$$\partial^2 f/\partial x \partial y = \partial^2 f/\partial y \partial x \quad \text{(commutation)}$$

- Total derivative:

$$\frac{df}{dx} = \frac{\partial f}{\partial x} + \frac{\partial f}{\partial y}\frac{dy}{dx}.$$



Line has slope $\frac{\partial f}{\partial x}(a,b)$

Graph of f(x,b)

Point (a,b,f(a,b))

$$\begin{aligned}\Delta f &= f(x+\Delta x, y+\Delta y) - f(x,y) \\ &= f(x+\Delta x, y+\Delta y) - f(x, y+\Delta y) \\ &\quad + f(x, y+\Delta y) - f(x,y) \\ &= \Delta x \left(\frac{\partial f}{\partial x}\right)_y + \Delta y \left(\frac{\partial f}{\partial y}\right)_x\end{aligned}$$

Useful Operators

$$f:\mathbb{R}^3\to\mathbb{R}, \vec{v}:\mathbb{R}^3\to\mathbb{R}^3$$

梯度 $\text{Gradient: } \nabla f \equiv \left(\frac{\partial f}{\partial x_1}, \frac{\partial f}{\partial x_2}, \frac{\partial f}{\partial x_3}\right)$

散度 $\text{Divergence: } \nabla\cdot\vec{v} \equiv \frac{\partial v_1}{\partial x_1}+\frac{\partial v_2}{\partial x_2}+\frac{\partial v_3}{\partial x_3}$

旋度 $\text{Curl: } \nabla\times\vec{v} \equiv \left(\frac{\partial v_3}{\partial x_2}-\frac{\partial v_2}{\partial x_3}, \frac{\partial v_1}{\partial x_3}-\frac{\partial v_3}{\partial x_1}, \frac{\partial v_2}{\partial x_1}-\frac{\partial v_1}{\partial x_2}\right)$

拉普拉斯算子
(梯度的散度) $\text{Laplacian: } \nabla^2 f \equiv \frac{\partial^2 f}{\partial x_1^2}+\frac{\partial^2 f}{\partial x_2^2}+\frac{\partial^2 f}{\partial x_3^2}$

Specific heat at constant volume

When the temperature changes from T to T+ΔT and the volume changes from V to V+ΔV, change in the internal energy U(T,V) is:

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

From the first law we have:

$$\Delta U = \Delta Q - P\,\Delta V$$

Let's first keep the volume constant ($\Delta V=0$) to derive the heat capacity. With $\Delta Q=\Delta U=0$, and from above that $\Delta U= \Delta T(\partial U/\partial T)_V$, so we have $(\partial U/\partial T)_V=\Delta Q/\Delta T$. This value means the amount of heat one needs to increase unit temperature of a substance, called the *specific heat at constant volume* (C_V).

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V$$

Fundamental relations in thermodynamics

Consider a Carnot cycle, the total amount of work done by the gas in a reversible cycle is ΔQ(ΔT/T), where ΔQ is the amount of heat energy added. From *geometry* of right bottom plot, we know that from

$$\Delta V\,\Delta P = \Delta Q\left(\frac{\Delta T}{T}\right)$$

$$\frac{\Delta T}{T}\cdot\left(\begin{array}{c}\text{heat needed}\\ \text{to change } V\\ \text{by } \Delta V\end{array}\right)_{\text{constant } T} = \Delta V\cdot\left(\begin{array}{c}\text{change in } P\\ \text{when } T \text{ changes}\\ \text{by } \Delta T\end{array}\right)_{\text{constant } V}$$

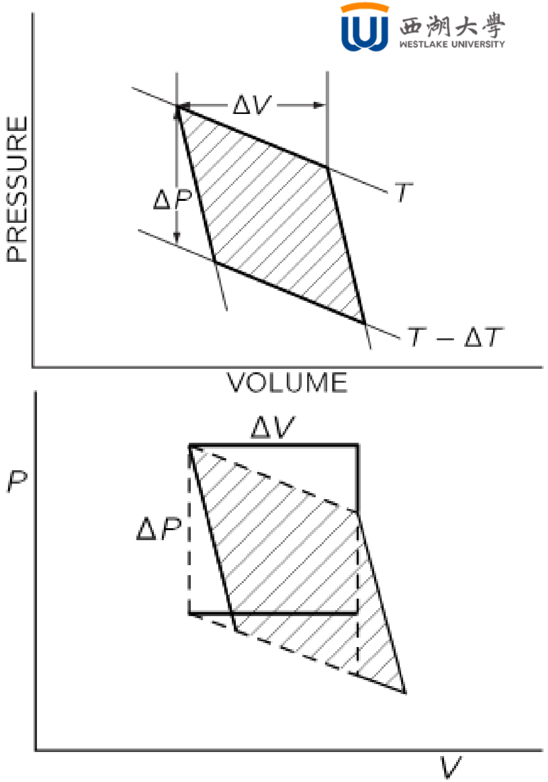
The heat needed to expand: $\Delta Q = T\left(\frac{\partial P}{\partial T}\right)_V \Delta V$

ΔU can be written as the sum of ΔQ and the work done: $\Delta U = T\left(\frac{\partial P}{\partial T}\right)_V \Delta V - P\,\Delta V$

Now we find the rate of change of U with V at constant T:

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

Only P, V, U, T appear in this fundamental equation, and can be used to deduce other thermodynamic results.



P-V diagrams for a Carnot cycle

Ideal gas at constant temperature

Assume we have an ideal gas at constant temperature T, so $\Delta U=0$ as U only depend on T. So we have

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

From integration (we write out "*const V*" as a reminder) we have

$$\begin{aligned} \ln P &= \ln T + \text{const}; \quad \text{const } V, \\ P &= \text{const} \times T; \quad \text{const } V. \end{aligned}$$

This agrees with the ideal gas law that PV=NkT. Recall that at one stage we assumed that the kinetic energy of the molecules was proportional to the temperature, which we call it the **ideal gas scale**, or **kinetic temperature.**

Here from the Second Law we defined we define the **grand thermodynamic absolute temperature**, which based on the Carnot cycles it is completely independent of the working substance, but rather the fundamental rule of thermodynamic.

It's nice to have the two temperature scales unified!

Enthalpy

Recall that $\Delta U = \Delta Q - P\Delta V$; we can play a trick to replace PΔV with VΔP.
Let's define a new state variable H called **enthalpy (焓),** its dictionary definition is the total heat content of a system, most used by chemists. Observe that $d(PV) = PdV + VdP$:

$$\begin{array}{rll} \Delta(PV) & = P\,\Delta V + V\,\Delta P & \\ \Delta U & = \Delta Q \quad - P\,\Delta V & \\ \hline \Delta(U + PV) & = \Delta Q \quad + V\,\Delta P & \end{array}$$

So now we have $\Delta H = \Delta Q + V\Delta P$, compared with ΔU, we have the following rules:
$U \to H$, $P \to -V$, $V \to P$. The fundamental relationship becomes

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

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

Similarly, we can show that the heat capacity at constant pressure is

$$\left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\mathrm{p}} = \mathrm{C}_{\mathrm{p}}$$

Helmholtz free energy

Helmholtz Free Energy **F** is a thermodynamic potential that measures the "useful" work obtainable from a closed thermodynamic system at a constant temperature and volume. The derivation is very similar to the last slide, from d(TS)=TdS+SdT, s.t.

$$dU=d(TS)-SdT-PdV$$

$$d(U-TS)=-SdT-PdV$$

We define a new variable F=U-TS and have the relation of dF=-SdT-PdV. From that, we can also derive the fundamental relationship involving F, like expressions for entropy and pressure:

$$S=-\left(\frac{\partial F}{\partial T}\right)\bigg|_V \qquad P=-\left(\frac{\partial F}{\partial V}\right)\bigg|_T$$

Clausius-Clapeyron equation

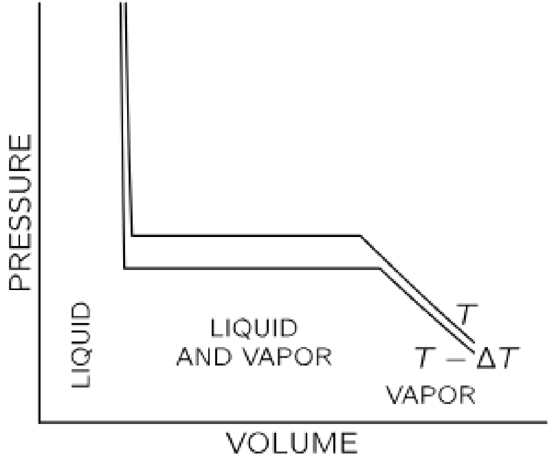
*Previously, we derived work done $= \Delta Q\left(\frac{\Delta T}{T}\right)$

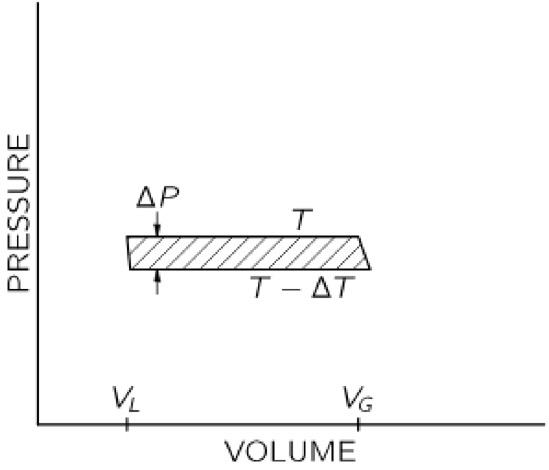
- Consider some liquid (so not ideal gas) in a cylinder, if we keep the temperature constant, we have an isothermal line on the P-V diagram which involves the phase change between liquid and gas.
- Now connect the two isothermal lines with adiabatic lines, the heat added to the substance in changing it from a liquid to a vapor is related to the work done by the substance as it goes around the cycle.
- Such heat is usually called the **Latent heat**, denoted by **L**. Using the analogy of the previous Carnot's argument*, we can now equate $L(\Delta T/T)$ and $\Delta P(V_G - V_L)$ [see bottom plot]. Similarly to previous example, we write

$$\frac{L}{T(V_G - V_L)} = (\partial P_{\text{vap}}/\partial T)$$

- For each mole, $V_G - V_L \approx V_G = RT/P$, and hence $\partial P/\partial T = PL/RT^2$. So the solution is in the form of $P = \text{const}\ e^{-L/RT}$, which is very similar to the results from kinematic theory

$$n = \left(\frac{1}{V_a}\right) e^{-(U_G - U_L)/RT} \longrightarrow P = nkT = \left(\frac{kT}{V_a}\right) e^{-(U_G - U_L)/RT}$$





Clausius-Clapeyron equation (cont)

Thermodynamics

(exact, universal; differential)

$$\frac{L}{T(V_G - V_L)} = (\partial P_{\text{vap}}/\partial T)$$

$$P = const\ e^{-L/RT}$$

Kinetic theory

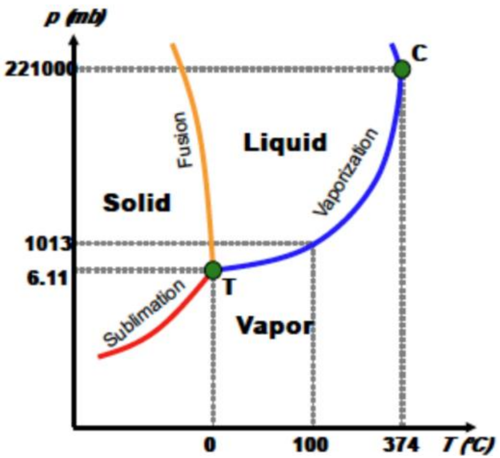
(approximation, limited; complete)

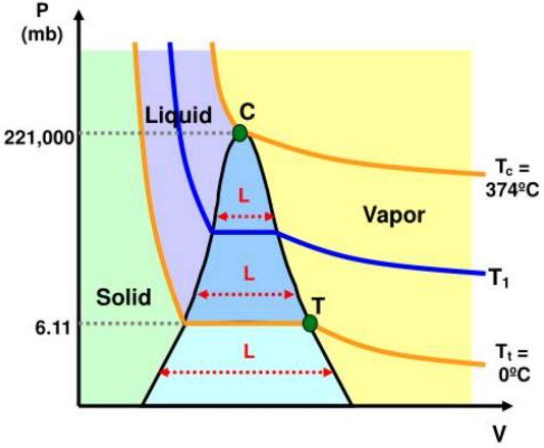
$$P = \left(\frac{kT}{V_a}\right) e^{-(U_G - U_L)/RT}$$

Not exactly the same if L=const

If this U_G-U_L is constant, independent of temperature, then the two **P-T** relations are equivalent. Since the pressure is constant while the volume is changing, the change in internal energy $U_G - U_L$ is equal to the heat L put in minus the work done $P(V_G - V_L)$, so $L=(U_G+PV_G)-(U_L+PV_L)$ or $L=H_G-H_L= \Delta H$.

1. In the phase change, the enthalpy plays the role of internal energy.
2. Unlike ideal gas energy states, which is purely a state of temperature, states of evaporation also depend on the pressure.
3. From thermodynamic relation, this the argument is true for any other change of state, i.e., solid-to-liquid: $(\partial P_{melt}/\partial T)_V = \mathbf{M}/[T(V_{liq} - V_{solid})]$





Heat capacities, latent heats, Gibbs energy

(in terms of entropy)

- For reversible process, we can express heat capacities in terms of entropy:

  $C_V = (\frac{dQ}{dT})_V = T(\frac{dS}{dT})_V$ and likewise, $C_P = T(\frac{dS}{dT})_P$

- For latent heat (heat needed to convert unit mole from one phase to another) the expression is L= ΔQ = TΔS. We can see that the heat exchange in the phase change comes from the change of entropy, even T and P can stay constant.

- Now equate $L=(U_G+PV_G)-(U_L+PV_L)$ and is $L= T (S_G-S_L)$ and rearrange, and define a new expression called **Gibbs free energy***, G=H-TS:

$$G_G=(U_G+PV_G) -TS_G= U_L+PV_L-TS_L=G_L$$

*constant T and P

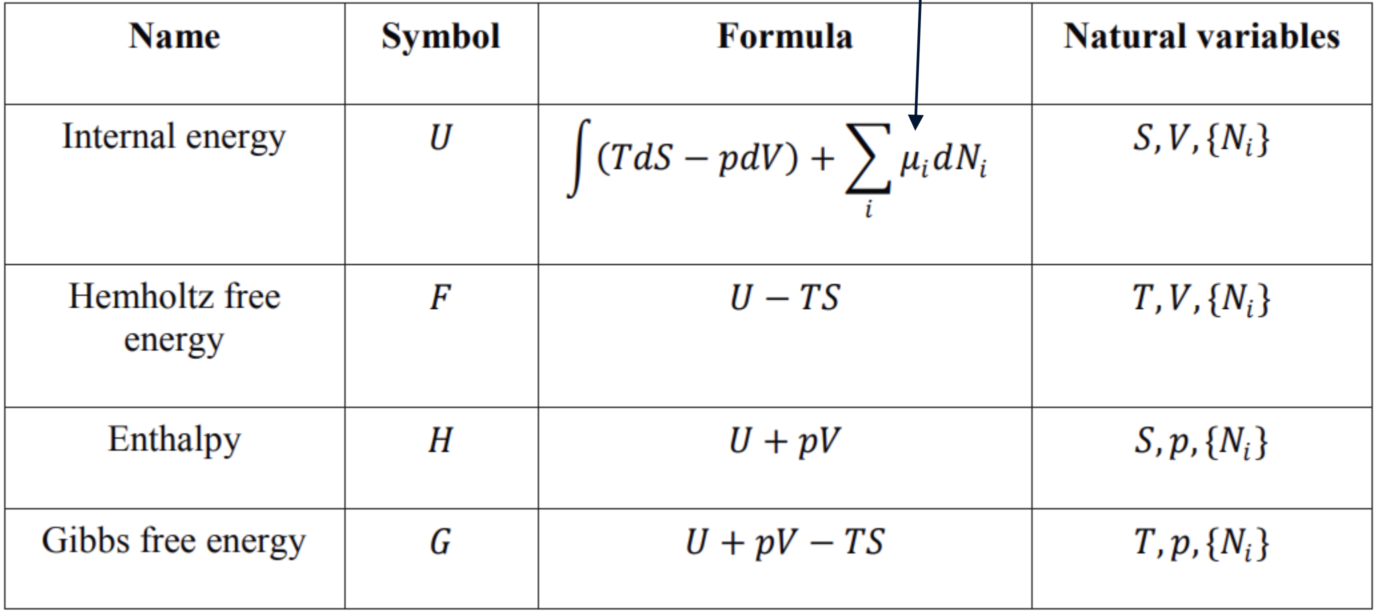
	Boiling Point Bpt/K	Heat of Vap. (kJ/mol)	ΔS of Vap. (J/K/mole)
H_2	20	0.46	23
Ne	27	1.7	63
Butane C_4H_{10}	273	21	77
NH_3	240	23	97
H_20	373	41	109
Al	2792	294	105
Fe	3134	340	108

Latent heat and entropy change for changes in different substances.

Gibbs free energy is, again, a thermodynamic **state variable** to predict spontaneous chemical reactions (ΔG<0).

Summary of state variables

$$\mu = \left(\frac{\partial F}{\partial N}\right)\bigg|_{T,V}$$



Name	Symbol	Formula	Natural variables
Internal energy	U	$\int (TdS - pdV) + \sum_i \mu_i dN_i$	$S, V, \{N_i\}$
Hemholtz free energy	F	$U - TS$	$T, V, \{N_i\}$
Enthalpy	H	$U + pV$	$S, p, \{N_i\}$
Gibbs free energy	G	$U + pV - TS$	$T, p, \{N_i\}$