



General Physics I

Lect.21 State Variables

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Variables in thermodynamics

- The subject of thermodynamics is complicated because there are so many different ways of describing the same thing.
- For a gas, ideal gas law $PV=NkT$, we can say pressure depends on the temperature and on the volume $P(V,T)$, or 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 as we like, such as: $U-TS$.
- For simplicity, we consider variables \mathbf{T} and \mathbf{V} , and their dependent functions \mathbf{U} and the \mathbf{P} . Everything else should be a function of them.
- Since the variable of P depend on V and T , ordinary derivative dP/dT is not enough. We define a new math symbol called partial derivative, $\partial P/\partial T$. This remind 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, $(\partial P/\partial T)_V$

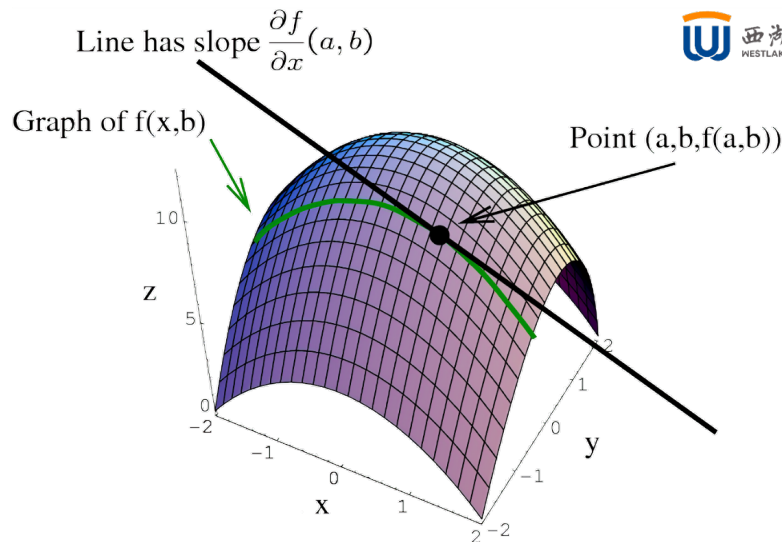
Partial differentials

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

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

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

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



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

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

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

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

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

$$\text{Laplacian: } \nabla^2 f \equiv \frac{\partial^2 f}{\partial x_1^2} + \frac{\partial^2 f}{\partial x_2^2} + \frac{\partial^2 f}{\partial x_3^2}$$

Specific heat at constant volume

When the temperature changes from T to $T+\Delta T$ and the volume changes from V to $V+\Delta V$, 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 $\Delta Q(\Delta T/T)$, where ΔQ is the amount of heat energy added. From *geometry* of right bottom plot, we know that from

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

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

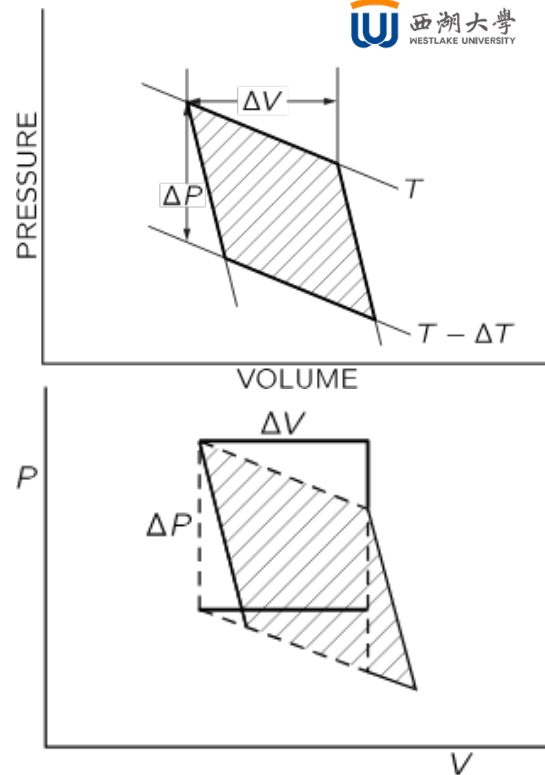
The heat needed to expand: $\Delta Q = T \left(\frac{\partial P}{\partial T} \right)_V \Delta V$

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

$$\ln P = \ln T + \text{const}; \quad \text{const } V,$$

$$P = \text{const} \times T; \quad \text{const } V.$$

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 define 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 $P\Delta V$ with $V\Delta P$.

Let's define a new state variable called **enthalpy (焓)**, its dictionary definition is the total heat content of a system, most used by chemists. Observe that

$d(PV) = PdV + VdT$:

$$\begin{aligned} \Delta(PV) &= P \Delta V + V \Delta P \\ \frac{\Delta U = \Delta Q - P \Delta V}{\Delta(U + PV) = \Delta Q + V \Delta P} \end{aligned}$$

So now we have $\Delta H = \Delta Q + V\Delta P$, compared with ΔU , we have the following rules:

$U \rightarrow H$, $P \rightarrow -V$, $V \rightarrow P$. The fundamental relationship becomes

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

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

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

Helmholtz free energy

Helmholtz Free Energy 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, where $d(TS)=TdS+SdT$, 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, compared with $dU=TdS-PdV$, we can use the rules $U\rightarrow F$, $S\rightarrow T$, $T\rightarrow -S$ to derive the fundamental relationship involving F .

One can find expressions for entropy and pressure:

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

Clausius-Clapeyron equation

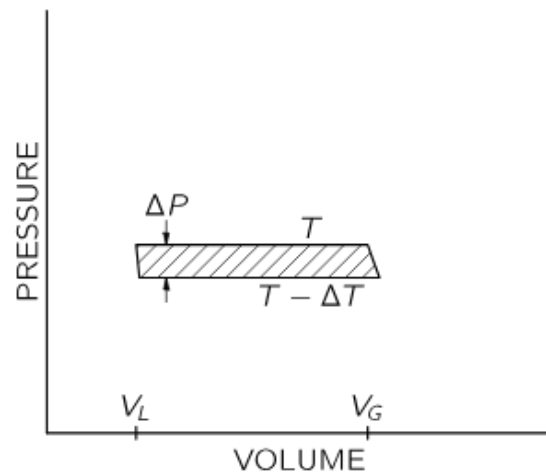
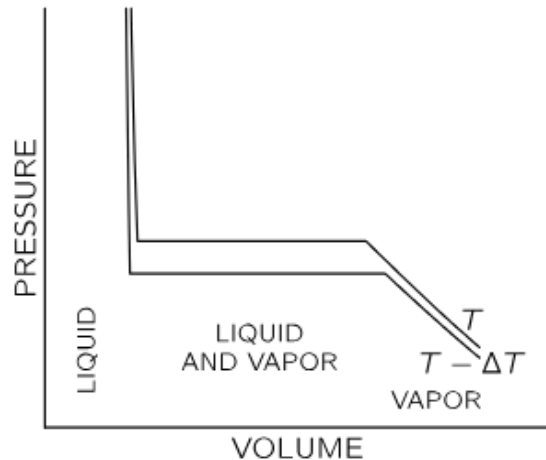
*Previously, we derived work done = $\Delta Q \left(\frac{\Delta T}{T} \right)$

- 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 involve 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 $\partial P / \partial T = L / (RT^2/P)$. So the solution is in the form of $P = \text{const } e^{-L/RT}$, which is very similar to the results from the result derived 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)

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

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

Kinetic theory

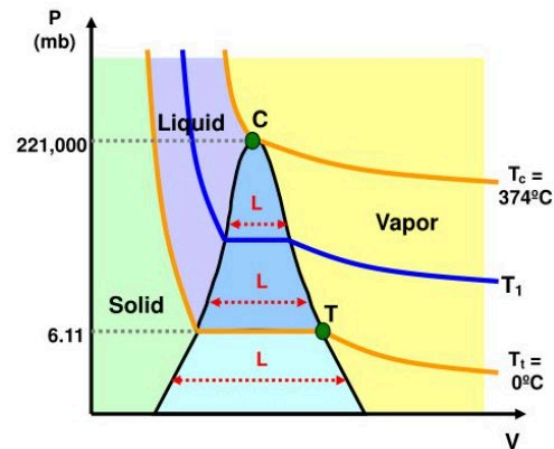
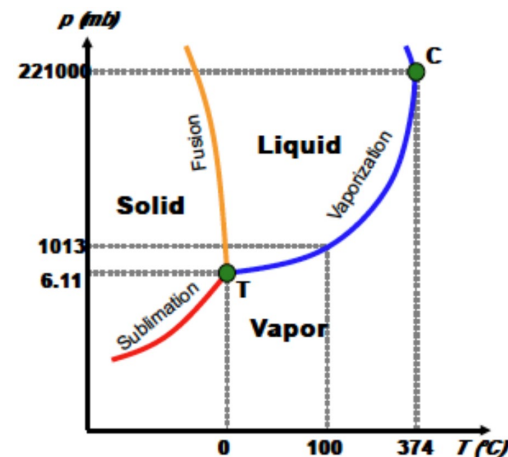
(approximation, limited; complete)

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

Not exactly the same if $L = \text{const}$

Rather, $U_G - U_L$ is constant, independent of temperature, then the two P - T relations are equal. 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 is purely a state of temperature, states of evaporation also depends on the pressure (see xenon).
3. From thermodynamic relation, this the argument is true for any other change of state, i.e., solid-to-liquid: $(\partial P_{\text{melt}} / \partial T)_V = \mathbf{M} / [T(V_{\text{liq}} - V_{\text{solid}})]$



Heat capacities, latent heats, Gibbs energy

(in terms of entropy)

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

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

- For latent heat (heat needed to convert unit mole from one phase to another) the expression is $L = \Delta Q = T\Delta S$. We can see that the heat exchange in the phase change comes from the change of entropy, even T and P can stay at 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*, $G = H - TS$:

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

*depends on T and P

	Bpt/K	Heat of Vap. (kJ/mol)	ΔS of Vap. (J/K/mole)
H₂	20	0.46	23
Ne	27	1.7	63
Butane	273	21	77
NH₃	240	23	97
H₂O	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 ($\Delta G < 0$).

Entropy for ideal gas

- For ideal gas, assuming constant number of molecules, we have, and we define a new quantity, heat capacity per mole, $C_{V,m} = C_V/n$, s.t.

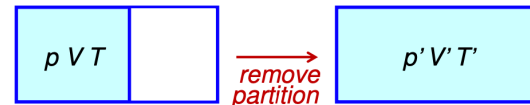
$$dU = TdS - PdV = nC_{V,m}dT$$

$$\begin{aligned} dS &= (dU + PdV)/T = (nC_{V,m}dT + PdV)/T \\ &= (nC_{V,m}dT + nRTdV/V)/T \\ &= n(C_{V,m}dT/T + RdV/V) \end{aligned}$$

$$S = nC_{V,m} \ln T + nR \ln(V/n) + \text{const.}$$

- The constant term we cannot directly derive from thermodynamical analysis (though we can probably guess it's proportional to n).
- Setting $S=0$, we have the adiabatic process, so $C_{V,m} \ln T_1 + R \ln V_1 = C_{V,m} \ln T_2 + R \ln V_2$
- We can show that $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

Back to the example in the last lecture, the expansion of gas into vacuum: $\Delta U = \Delta Q = \Delta W = 0$



$\Delta U = 0$, $\Delta T = 0$ for an ideal gas
 $T = T'$.

Per mole of gas we have

$$\begin{aligned} \Delta S &= C_V \ln(T/T') + R \ln(V/V') \\ &= R \ln(V/V') > 0 \text{ for } V' > V \end{aligned}$$

Summary of state variables

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

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	$U + pV - TS$	$T, p, \{N_i\}$