Partial Derivative Games in Thermodynamics

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1 Mathematics

1.1 Chain rule review

Suppose $z = z(x, y)$, $x = x(s, t)$, $y = y(s, t)$ and compute $\frac{\partial z}{\partial s}$ and $\frac{\partial z}{\partial t}$.

From $z = z(x, y)$ we have:

$$dz = \frac{\partial z}{\partial x} dx + \frac{\partial z}{\partial y} dy.$$

now we do the same thing to dx, dy:

$$dx = \frac{\partial x}{\partial s} ds + \frac{\partial x}{\partial t} dt.$$

$$dy = \frac{\partial y}{\partial s} ds + \frac{\partial y}{\partial t} dt.$$

plug into dz:

$$dz = \Big(\frac{\partial z}{\partial x}\frac{\partial x}{\partial s} + \frac{\partial z}{\partial y}\frac{\partial y}{\partial s}\Big) ds + \Big(\frac{\partial z}{\partial x}\frac{\partial x}{\partial t} + \frac{\partial z}{\partial y}\frac{\partial y}{\partial t}\Big) dt$$

therefore

$$\frac{\partial z}{\partial s} = \frac{\partial z}{\partial x}\frac{\partial x}{\partial s} + \frac{\partial z}{\partial y}\frac{\partial y}{\partial s}.$$

$$\frac{\partial z}{\partial t} = \frac{\partial z}{\partial x}\frac{\partial x}{\partial t} + \frac{\partial z}{\partial y}\frac{\partial y}{\partial t}.$$

To be more specific about the variables, we can write:

$$\Big(\frac{\partial z}{\partial s}\Big)_t = \Big(\frac{\partial z}{\partial x}\Big)_y\Big(\frac{\partial x}{\partial s}\Big)_t + \Big(\frac{\partial z}{\partial y}\Big)_x\Big(\frac{\partial y}{\partial s}\Big)_t.$$

$$\Big(\frac{\partial z}{\partial t}\Big)_s = \Big(\frac{\partial z}{\partial x}\Big)_y\Big(\frac{\partial x}{\partial t}\Big)_s + \Big(\frac{\partial z}{\partial y}\Big)_x\Big(\frac{\partial y}{\partial t}\Big)_s.$$

The subscript indicates which variable is to be held constant.

1.2 Multivariable derivatives

f, g, h are all functions of x, y, that is: $f = f(x, y), g = g(x, y), h = h(x, y)$

$$\Big(\frac{\partial f}{\partial g}\Big)_h = 1 \Big/ \Big(\frac{\partial g}{\partial f}\Big)_h \tag{1}$$

This is obvious once rewrite functions as: $f = f(g, h)$.

$$\left(\frac{\partial f}{\partial g}\right)_x = \frac{\partial f}{\partial y} \Big/ \frac{\partial g}{\partial y} \tag{2}$$

Proof:

We can rewrite $f = f(x, y) = f(x, y(x, g)) \Rightarrow f(x, g)$, therefore:

$$\left(\frac{\partial f}{\partial g}\right)_x = \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial g}\right)_x = \frac{\partial f}{\partial y} \Big/ \frac{\partial g}{\partial y}.$$

Note that the DOF remains 2

$$\left(\frac{\partial y}{\partial x}\right)_f = -\frac{\partial f}{\partial x} \Big/ \frac{\partial f}{\partial y} \tag{3}$$

Proof:

If we hold f as a constant, then x, y are no longer independent since they're now related by $f = f(x, y)$.

$$df \equiv 0 = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy \quad \Rightarrow \quad \frac{\partial f}{\partial x} dx = -\frac{\partial f}{\partial y} dy.$$

since x, y are related, we can write $y = y(x, f)$, which leads to:

$$dy = \left(\frac{\partial y}{\partial x}\right)_f dx + \left(\frac{\partial y}{\partial f}\right)_x df = \left(\frac{\partial y}{\partial x}\right)_f dx + 0.$$

compare two equations above, we then arrive at:

$$\frac{\partial y}{\partial x} = -\frac{\partial f}{\partial x} \Big/ \frac{\partial f}{\partial y}.$$

Q.E.D

*Cyclic chain rule:

$$\left(\frac{\partial f}{\partial g}\right)_h \left(\frac{\partial g}{\partial h}\right)_f \left(\frac{\partial h}{\partial f}\right)_g = -1 \tag{4}$$

Proof:

WLOG, we look at $\left(\frac{\partial h}{\partial f}\right)_g$ first, where g is held constant. Since $g = g(h, f)$, h, f become dependent variables once g is fixed:

$$dg \equiv 0 = \left(\frac{\partial g}{\partial h}\right)_f dh + \left(\frac{\partial g}{\partial f}\right)_h df \quad \Rightarrow \quad df = -\left(\frac{\partial g}{\partial h}\right)_f \left(\frac{\partial f}{\partial g}\right)_h dh.$$

Therefore:

$$\left(\frac{\partial f}{\partial h}\right)_g = -\left(\frac{\partial g}{\partial h}\right)_f \left(\frac{\partial f}{\partial g}\right)_h \quad \Rightarrow \quad \left(\frac{\partial f}{\partial g}\right)_h \left(\frac{\partial g}{\partial h}\right)_f \left(\frac{\partial h}{\partial f}\right)_g = -1.$$

Q.E.D

$$\left(\frac{\partial f}{\partial x}\right)_g = \frac{\partial f}{\partial x} + \frac{\partial f}{\partial y}\left(\frac{\partial y}{\partial x}\right)_g \qquad (5)$$

Proof:

Similarly, apply chain rule to $f = f(x, y) = f(x(x), y(x, g))$, where x is itself the parameter:

$$\left(\frac{\partial f}{\partial x}\right)_g = \frac{\partial f}{\partial x}\frac{\partial x}{\partial x} + \frac{\partial f}{\partial y}\left(\frac{\partial y}{\partial x}\right)_g = (5).$$

Q.E.D

1.3 Practice: 1st Law of Thermodynamics

First, look at two useful concepts, i.e. the heat capacity C, under different circumstances, it can be C_v or C_p.

$$C = \lim_{T \to 0}\frac{Q}{\Delta T}.$$

If the volume is fixed, $pdV = 0$, then

$$Q = U_f - U_i = \Delta U.$$

therefore:

$$C_v = \lim_{\Delta T \to 0}\frac{\Delta U}{\Delta T} = \left(\frac{\partial U}{\partial T}\right)_V.$$

On the other hand, if the pressure is fixed, the work on the system is $W = -PdV$, then:

$$Q = \Delta U - W = \Delta U + P\Delta V.$$

therefore:

$$C_p = \lim_{T \to 0}\frac{\Delta U + p\Delta V}{\Delta T} = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P.$$

or, in terms of enthalpy: $H = U + PV$, it becomes

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P, \quad Q = \Delta H.$$

Now we play with these equations. Note that in C_v, the independent variables we chose are T, V, whereas in C_p they are P, T. If we were to study the connection between C_v and C_p, we have to express them under the same set of variables.

If there exists an equation of state $F(P, V, T) = 0$ (generically there is, e.g. $PV = nRT$), this can be achieved by writing $U = U(T, V) = U(T, V(T, P))$. Then the partial derivative becomes:

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P \qquad (6)$$

where the last term $\left(\frac{\partial V}{\partial T}\right)_P$ encodes information of equation of state.

Using this, we can rewrite C_p as:

$$\begin{aligned}
C_p &= \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \\
&= \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \qquad (7) \\
&= \left(\frac{\partial V}{\partial T}\right)_P\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] + C_v
\end{aligned}$$

or

$$C_p - C_v = \left(\frac{\partial V}{\partial T}\right)_P\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right].$$

One can check that for ideal gas, it becomes the famous $C_p - C_v = nR$.
From (7) we can solve for $\left(\frac{\partial U}{\partial V}\right)_T$:

$$\left(\frac{\partial U}{\partial V}\right)_T = (C_p - C_v)\left(\frac{\partial T}{\partial V}\right)_P - P \qquad (8)$$

Why we are interested in this tedious expression? Well, if we choose T, V to be the set of independent variables, and if C_p, C_v and the Eq of state can be measured experimentally, this will be extremely useful in finding the differential of $U(T, V)$:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad (9)$$

plug in (8) into (9):

$$dU = C_v dT + \left[(C_p - C_v)\left(\frac{\partial T}{\partial V}\right)_P - P\right]dV \qquad (10)$$

which makes it possible to derive the internal energy by a path integral:

$$U = U_0 + \int_{\partial(T,V)} \left\{C_v dT + \left[(C_p - C_v)\left(\frac{\partial T}{\partial V}\right)_P - P\right]dV\right\} \qquad (11)$$

where $\partial(T, V)$ represents the path in $T - V$ parameter space.
But what if we want it represented in P, V, since sometimes we'd like to analyze things in $P - V$ diagram more than $T - V$. Well, we can use the equation of state and derive the following:

$$dT = \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV.$$

and plug this into (11):

$$dU = C_v\left(\frac{\partial T}{\partial P}\right)_V dP + \left[C_p\left(\frac{\partial T}{\partial V}\right)_P - P\right]dV \qquad (12)$$

We can use (12) to study adiabatic process, where $Q = 0$ thus $S = Const.$ this means:

$$dU + PdV = 0.$$

therefore

$$C_v\left(\frac{\partial T}{\partial P}\right)_V dP + C_p\left(\frac{\partial T}{\partial V}\right)_P dV = 0 \qquad (13)$$

simplify by applying cyclic chain rule:

$$\left(\frac{\partial P}{\partial V}\right)_S = \frac{C_p}{C_v}\left(\frac{\partial P}{\partial V}\right)_T \equiv \gamma\left(\frac{\partial P}{\partial V}\right)_T.$$

For ideal gas, this indicates the $P-V$ lines are steeper in adiabatic process than in isotherms, but may differ in other equations of state.

Now suppose the equation of state is given by:

$$PV = F(T).$$

where F(T) may be some complicated function of T or ideal gas's $PV = nRT$. Therefore, after taking derivative of P, V respectively, we have:

$$V = \frac{dF}{dT}\left(\frac{\partial T}{\partial P}\right)_V, \quad P = \frac{dF}{dT}\left(\frac{\partial T}{\partial V}\right)_P.$$

plug this into (13) we have:

$$C_v V\, dP + C_p P\, dV = 0 \quad \Rightarrow \quad \frac{dP}{P} + \gamma\frac{dV}{V} = 0 \tag{14}$$

Therefore, in an adiabatic process:

$$PV^\gamma = C \tag{15}$$