# Math Diversion 739

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> Zathras is used to being beast of burden to other
> people's needs. Very sad life... Probably have
> very sad death. But, at least
> there is symmetry.
> —Zathras (a character on Babylon 5)

The material is found at:[1]

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Source: American Journal of Physics (AJP), Vol. 27 (May 1959),
       pp 302--306
Title: Systematic Approach to the Calculation of Thermodynamic
       Transforms
 Presenter:  Charles W. Carroll
 Notes prepared by Patrick
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## 1 Preliminaries

$$\text{coef. of (isothermal) compressibility,} \qquad k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T ; \tag{1}$$

$$\text{coef. of expansion,} \qquad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P ; \tag{2}$$

$$\text{coef. of pressure,} \qquad \pi = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V . \tag{3}$$

According to Copilot, for clarity, $k$ should be subscripted as $k_T$ these days, though it would not have been the habit of writers to do so in the 1950s.

$$\left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{\left(\frac{\partial x}{\partial y}\right)_z} . \tag{4}$$

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[1] I took these notes a number of years ago, directly from the AJP volume, which I no longer have access to; so I have no way to double check the accuracy of my notes.

This last equation makes sense because in a system of three interrelated variables, if one of them is held fixed, then the remaining two unfixed variables comprise a system of only two variables, putting us in the realm of 'ordinary derivatives'.

$$\left(\frac{\partial y}{\partial x}\right)_z = -\frac{\left(\frac{\partial z}{\partial x}\right)_y}{\left(\frac{\partial z}{\partial y}\right)_x} \,. \tag{5}$$

If

$$dz = M dx + N dy \,, \tag{6}$$

then

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \,. \tag{7}$$

If

$$z = z(x(t,u), y(t,u)) \tag{8}$$

then

$$\left(\frac{\partial z}{\partial t}\right)_u = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial t}\right)_u + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial t}\right)_u \,, \tag{9}$$

If

$$z = z(x(u), y(u)) \tag{10}$$

then if we hold $x$ constant then $u = u(y)$ and $z = z(u(y))$.

$$\left(\frac{\partial z}{\partial t}\right)_u = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial t}\right)_u + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial t}\right)_u \,, \tag{11}$$

then

$$\left(\frac{\partial z}{\partial y}\right)_x = \left(\frac{\partial z}{\partial u}\right)_x \left(\frac{\partial u}{\partial y}\right)_x \,, \tag{12}$$

$$\left(\frac{\partial x}{\partial u}\right)_y = \frac{\partial(x,y)}{\partial(u,y)} \,. \tag{13}$$

Hence we have the equation for Jacobians.

$$J\left(\frac{x,y}{z,w}\right) J\left(\frac{z,w}{u,v}\right) = J\left(\frac{x,y}{u,v}\right) \,. \tag{14}$$

Now for the differentials:

$$dU = TdS - PdV \,, \tag{15a}$$

$$dH = TdS + VdP \,, \tag{15b}$$

$$dG = -SdT + VdP \,, \tag{15c}$$

$$dA = -SdT - PdV \,. \tag{15d}$$

Next, an important Maxwell relation:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \,. \tag{16}$$

## 2 Into the Breach

Now, the specific heat at constant volume:

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \ . \tag{17}$$

Therefore

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \, . \tag{18}$$

Similarly, with

$$dH = TdS + VdP \, , \tag{19}$$

and with

$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P = C_P \, , \tag{20}$$

and we get

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \, . \tag{21}$$

Synthesizing prior results, we have that

$$\begin{aligned}\left(\frac{\partial P}{\partial S}\right)_V &= \frac{1}{\left(\frac{\partial S}{\partial P}\right)_V} = \frac{1}{\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V} \\ &= \frac{1}{\frac{C_V}{T}\left(\frac{\partial T}{\partial P}\right)_V} = \frac{TP\pi}{C_V} \, . \end{aligned} \tag{22}$$

We can also work out:

$$\begin{aligned}\left(\frac{\partial P}{\partial V}\right)_S &= -\frac{\left(\frac{\partial S}{\partial V}\right)_P}{\left(\frac{\partial S}{\partial P}\right)_V} = -\frac{\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P}{\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V} \\ &= -\frac{C_P P\pi}{C_V V\beta} \, . \end{aligned} \tag{23}$$

Likewise,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{TP\pi}{C_V} \, . \tag{24}$$

Onward!

$$\begin{aligned}\left(\frac{\partial H}{\partial P}\right)_T &= T\left(\frac{\partial S}{\partial P}\right)_T + V \\ &= T\left(\frac{\partial V}{\partial T}\right)_P + V \\ &= V(1 - T\beta) \, . \end{aligned} \tag{25}$$

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Given

$$H = U + PV\,, \tag{26}$$

then

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial T}\right)_V\,, \tag{27}$$

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$$\begin{aligned}
\left(\frac{\partial H}{\partial T}\right)_V &= \left(\frac{\partial H}{\partial P}\right)_V \left(\frac{\partial P}{\partial T}\right)_V \\
&= \left[T\left(\frac{\partial S}{\partial P}\right)_V + V\right]\left(\frac{\partial P}{\partial T}\right)_V \\
&= T\left(\frac{\partial S}{\partial P}\right)_V + V\left(\frac{\partial P}{\partial T}\right)_V \\
&= C_V + V\pi P\,. \qquad (28)
\end{aligned}$$

Similarly,

$$\left(\frac{\partial A}{\partial P}\right)_T = Pk_T V\,. \tag{29}$$

Moving on,

$$\left(\frac{\partial H}{\partial V}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_P = \frac{C_P}{\beta V}\,, \tag{30}$$

and

$$\begin{aligned}
\left(\frac{\partial H}{\partial G}\right)_T &= \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial G}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T \Big/ \left(\frac{\partial G}{\partial P}\right)_T \\
&= \frac{T\left(\dfrac{\partial S}{\partial P}\right)_T + V}{V} = 1 - T\beta\,. \qquad (31)
\end{aligned}$$

Similarly,

$$\left(\frac{\partial U}{\partial G}\right)_T = kP(1 - T\pi)\,, \tag{32}$$

and

$$\left(\frac{\partial S}{\partial A}\right)_T = -\pi\,. \tag{33}$$

$$\begin{aligned}
\left(\frac{\partial A}{\partial T}\right)_G &= J\left(\frac{A,G}{T,G}\right) = J\left(\frac{A,G}{T,V}\right)\Big/ J\left(\frac{T,G}{T,V}\right) \qquad [J \text{ stands for Jacobian}] \\
&= \left\{-SV\left(\frac{\partial P}{\partial V}\right)_T - \left[(-P)\left(-S + V\left(\frac{\partial P}{\partial T}\right)_V\right)\right]\right\}\Big/ V\left(\frac{\partial P}{\partial V}\right)_T \\
&= kP(S - V\pi P) - S\,. \qquad (34)
\end{aligned}$$

Likewise,

$$\left(\frac{\partial H}{\partial G}\right)_S = \frac{C_P}{C_P - S\beta T}\,. \tag{35}$$

Hint:

$$J\left(\frac{H,S}{G,S}\right) = J\left(\frac{H,S}{P,T}\right)\Big/ J\left(\frac{G,S}{P,T}\right)\,. \tag{36}$$

## 3 Conclusion

Hopefully I didn't introduce any errors into the work. Also, we've been warned that both nomenclature and symbolism have changed somewhat in the field of thermodynamics since that of 1959. I made no effort to ferret those things out in all possible cases.