

Chapter 6: Putting the Second Law to Work

In the previous chapter, we saw that for a spontaneous process, $\Delta S_{\text{univ}} > 0$. While this is a useful criterion for determining whether or not a process is spontaneous, it is rather cumbersome, as it requires one to calculate not only the entropy change for the system, but also that of the surroundings. It would be much more convenient if there was a single criterion that would do the job and focus only on the system. As it turns out, there is!

Free Energy Functions

Since we know that

$$\Delta S_{\text{univ}} \geq 0$$

for any natural process, and

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

all we need to do is to find an expression for ΔS_{surr} that can be determined by the changes in the system itself. Fortunately, we have already done that! Recalling that at constant temperature

$$\Delta S = -\frac{q_{\text{rev}}}{T}$$

and at constant pressure

$$\Delta H = q_p$$

it follows that at constant temperature and pressure

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T}$$

Substitution into the above equations yields an expression for the criterion of spontaneity that depends only on variables describing the changes in the system!

$$\Delta S_{\text{univ}} \geq \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T}$$

So

$$\Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} \geq 0$$

Multiplying both sides by -T yields

$$\Delta H - T\Delta S \leq 0$$

A similar derivation for constant volume processes results in the expression (at constant volume and temperature)

$$\Delta U - T\Delta S \leq 0$$

The first expression is of greater use to chemists, as most of chemistry occurs at constant pressure. For geologists, however, who are interested in processes that occur at very high pressures (say, under the weight of an entire mountain) and expansion is not a possibility, the constant volume expression may be of greater interest.

All of the above arguments can be made for systems in which the temperature is not constant by considering infinitesimal changes. The resulting expressions are

$$dH - TdS \leq 0 \quad \text{and} \quad dU - TdS \leq 0$$

The Gibbs and Helmholtz Functions

The first expression suggests a very convenient thermodynamic function to help keep track of both the effects of entropy and enthalpy changes. This function, the **Gibbs function** (or **Gibbs Free Energy**) is defined by

$$G \equiv H - TS$$

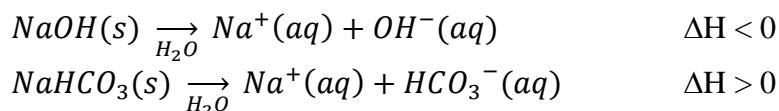
A change in the Gibbs function can be expressed

$$\Delta G = \Delta H - \Delta(TS)$$

Or at constant temperature

$$\Delta G = \Delta H - T\Delta S$$

And the criterion for a process to be spontaneous is the $\Delta G < 0$. As such, it should be clear spontaneity is not merely a function the enthalpy change (although exothermic processes tend to be spontaneous) but also a function of the entropy change, weighted by the temperature. Going back to an earlier example,



It is easy to see why both processes are spontaneous. In the first case, the process is exothermic (favorable) and proceeds with an increase in entropy (also favorable) due to the formation of fragments in the liquid phase (more chaotic) from a very ordered solid (more ordered). The second reaction is endothermic (unfavorable) but proceeds with an increase in entropy (favorable). So, so long as the temperature is high enough, the entropy term will overwhelm the enthalpy term and cause the process to be spontaneous.

The conditions for spontaneous processes at constant temperature and pressure can be summarized in the following table.

ΔH	ΔS	Spontaneous?
> 0	> 0	At high T
> 0	< 0	At no T
< 0	> 0	At all T
< 0	< 0	At low T

Similarly to the Gibbs function, the **Helmholtz function** is defined by

$$A \equiv U - TS$$

and provides another important criterion for spontaneous processes at constant value and temperature. At constant temperature, the Helmholtz function can be expressed by

$$\Delta A = \Delta U - T\Delta S$$

Based on similar arguments used for the Gibbs function, the Helmholtz function also can be used to predict which processes will be spontaneous at constant volume and temperature according to the following table.

ΔU	ΔS	Spontaneous?
> 0	> 0	At high T
> 0	< 0	At no T
< 0	> 0	At all T
< 0	< 0	At low T

Calculating ΔG for Reactions

Much like in the case of enthalpy (and unlike entropy), free energy functions do not have an unambiguous zero to the energy scale. So, just like in the case of enthalpies of formation, by convention, the standard free energy of formation (ΔG_f°) for elements in their standard states is defined as zero.

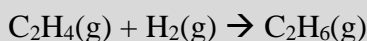
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This allows for two important things to happen. First, ΔG_f° can be measured and tabulated for any substance (in principle, at least.) ΔG_f° is determined to be $\Delta G_{\text{rxn}}^\circ$ for the reaction that forms one mole of a compound from elements in their standard states (similarly to how ΔH_f° is defined.)

Secondly, tabulated ΔG_f° can be used to calculate standard reaction free energies ($\Delta G_{\text{rxn}}^\circ$) in much the same way as ΔH_f° is used for reaction enthalpies.

Example 6.1:

Given the following data at 298 K, calculate ΔG° at 298 K for the following reaction:



Substance	ΔG_f° (kJ/mol)
$\text{C}_2\text{H}_4(\text{g})$	68.4
$\text{C}_2\text{H}_6(\text{g})$	-32.0

Solution:

The ΔG_f° values can be used to calculate ΔG° for the reaction in exactly the same method as ΔH_f° can be used to calculate a reaction enthalpy.

$$\Delta G^\circ = (1 \text{ mol})(-32.0 \text{ kJ/mol}) - (1 \text{ mol})(68.4 \text{ kJ/mol})$$

$$\Delta G^\circ = 100.4 \text{ kJ}$$

Note: $\text{H}_2(\text{g})$ is not included in the calculation since ΔG_f° for $\text{H}_2(\text{g})$ is 0 since it is an element in its standard state.

Combining the First and Second Laws

Modeling the dependence of the Gibbs and Helmholtz functions behave with varying temperature, pressure, and volume is fundamentally useful. But in order to do that, a little bit more development is necessary.

To see the power and utility of these functions, it is useful to combine the First and Second Laws into a single mathematical statement. In order to do that, one notes that since

$$dS = \frac{dq}{T}$$

for a reversible change, it follows that

$$dq = TdS$$

And since

$$dw = -pdV$$

for a reversible expansion in which only p-V work is done, it also follows that (since $dU = dq + dw$)

$$dU = TdS - pdV$$

This is an extraordinarily powerful result. This differential for dU can be used to simplify the differentials for H, A, and G. But even more useful are the constraints it places on the variables T, S, p, and V due to the mathematics of exact differentials!

Maxwell Relations

The above result suggests that the natural variables of internal energy are S and V (or the function can be considered as U(S, V)). So the total differential (dU) can be expressed:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

Also, by inspection (comparing the two expressions for dU) it is apparent that

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

But the value doesn't stop there! Since dU is an exact differential, the Euler relation must hold that

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V$$

By substituting the previous statements for $\left(\frac{\partial U}{\partial S}\right)_V$ and $\left(\frac{\partial U}{\partial V}\right)_S$, we see that

$$\left[\frac{\partial}{\partial V}(T)\right]_S = \left[\frac{\partial}{\partial S}(-p)\right]_V$$

or

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

This is an example of a **Maxwell Relation**. These are very powerful relationship that allows one to substitute partial derivatives when one is more convenient (perhaps it can be expressed entirely in terms of α and/or κ_T for example.)

A similar result can be derived based on the definition of H.

$$H \equiv U + pV$$

Differentiating (and using the chain rule on $d(pV)$ yields

$$dH = dU + pdV + Vdp$$

Making the substitution using the combined first and second laws ($dU = TdS - pdV$) for a reversible change involving on expansion (p-V) work

$$dH = TdS - pdV + pdV + Vdp$$

This expression can be simplified by canceling the pdV terms.

$$dH = TdS + Vdp$$

And much as in the case of internal energy, this suggests that the natural variables of H are S and p. Or

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$$

where

$$\left(\frac{\partial H}{\partial S}\right)_p = T \quad \text{and} \quad \left(\frac{\partial H}{\partial p}\right)_S = V$$

It is worth noting at this point that since $\left(\frac{\partial U}{\partial S}\right)_V = T$ and $\left(\frac{\partial H}{\partial S}\right)_p = T$ that

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p$$

But also, since the Euler Relation must also hold

$$\left[\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right)_p\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)_S\right]_p$$

So

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

This is the Maxwell relation on H. Maxwell relations can also be developed based on A and G. The results of those derivations are summarized in the table below.

Function	Differential	Natural Variables	Maxwell Relation
U	$dU = TdS - pdV$	S, V	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
H	$dH = TdS + Vdp$	S, p	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
A	$dA = -pdV - SdT$	V, T	$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
G	$dG = Vdp - SdT$	p, T	$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

The Maxwell relations are extraordinarily useful in deriving the dependence of thermodynamic variables on the state variables of p, T, and V.

Example 6.2:

Show that

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{\alpha}{\kappa_T} - p$$

Solution:

Start with the combined first and second laws:

$$dU = TdS - pdV$$

Divide both sides by dV and constraint to constant T:

$$\left.\frac{dU}{dV}\right|_T = T \left.\frac{dS}{dV}\right|_T - p \left.\frac{dV}{dV}\right|_T$$

Noting that

$$\left.\frac{dU}{dV}\right|_T = \left(\frac{\partial U}{\partial V}\right)_T, \left.\frac{dS}{dV}\right|_T = \left(\frac{\partial S}{\partial V}\right)_T, \text{ and } \left.\frac{dV}{dV}\right|_T = 1$$

The result is

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

Now, employ the Maxwell relation on A

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

to get

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

And since

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

It is apparent that

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{\alpha}{\kappa_T} - p$$

Note: How cool is that? This result was given without proof in chapter 4, but can now be proven analytically using the Maxwell Relations!

A, G and Maximum Work

The functions A and G are oftentimes referred to as **free energy** functions. The reason for this is that they are a measure of the maximum work (in the case of ΔA) or non p-V work (in the case of ΔG) that is available from a process. To show this, consider the total differentials.

First, consider the differential of A.

$$dA = dU - TdS - SdT$$

Substituting the combined first and second laws for dU, but expressing the work term as dw, yields

$$dA = TdS - dw - TdS - SdT$$

And cancelling the TdS terms gives

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$$dA = dw - SdT$$

or at constant temperature ($dT = 0$)

$$dA = dw$$

Since the only assumption made here was that the change is reversible (allowing for the substitution of TdS for dq), and dw for a reversible change is the maximum amount of work, it follows that dA gives the maximum work that can be produced from a process at constant temperature.

Similarly, a simple expression can be derived for dG . Starting from the total differential of G .

$$dG = dU + pdV + Vdp - TdS - SdT$$

Using an expression for $dU = dq + dw$, where $dq = TdS$ and dw is split into two terms, one (dw_{pV}) describing the work of expansion and the other (dw_e) describing any other type of work (electrical, stretching, etc.)

$$dU = TdS + dw_{pV} + dw_e$$

dG can be expressed as

$$dG = TdS - pdV + dw_e + pdV + Vdp - TdS - SdT$$

Cancelling the TdS and pdV terms leaves

$$dG = dw_e + Vdp - SdT$$

So at constant temperature ($dT = 0$) and pressure ($dp = 0$),

$$dG = dw_e$$

This implies that dG gives the maximum amount of non p-V work that can be extracted from a process.

This concept of dA and dG giving the maximum work (under the specified conditions) is where the term “free energy” comes from, as it is the energy that is *free* to do work in the surroundings. If a system is to be optimized to do work in the surroundings (for example a steam engine that may do work by moving a locomotive) the functions A and G will be important to understand. It will, therefore, be useful to understand how these functions change with changing conditions, such as volume, temperature, and pressure.

Volume Dependence of A

If one needs to know how the Helmholtz function changes with changing volume at constant temperature, the following expression can be used:

$$\Delta A = \int_{V_1}^{V_2} \left(\frac{\partial A}{\partial V} \right)_T dV$$

But how does one derive an expression for $\left(\frac{\partial A}{\partial V} \right)_T$? This is a fairly straight forward process that begins with the definition of A:

$$A = U - TS$$

Differentiating (and using the chain rule to evaluate d(TS)) yields

$$dA = dU - TdS - SdT$$

Now, it is convenient to use the combined first and second laws

$$dU = TdS - pdV$$

which assumes 1) a reversible change and 2) only pV work is being done. Substituting this into the expression above yields

$$dA = TdS - pdV - TdS - SdT$$

Canceling the TdS terms gives the important result

$$dA = -pdV - SdT$$

The natural variables of A are therefore V and T! So the total differential of A is conveniently expressed as

$$dA = \left(\frac{\partial A}{\partial V} \right)_T dV + \left(\frac{\partial A}{\partial T} \right)_V dT$$

And by inspection, it is clear that

$$\left(\frac{\partial A}{\partial V} \right)_T = -p \quad \text{and} \quad \left(\frac{\partial A}{\partial T} \right)_V = -S$$

And so, one can evaluate

$$\Delta A = \int_{V_1}^{V_2} \left(\frac{\partial A}{\partial V} \right)_T dV$$

as

$$\Delta A = - \int_{V_1}^{V_2} p dV$$

If the pressure is independent of the temperature, it can be pulled out of the integral. Otherwise, the temperature dependence of the pressure must be included. Fortunately, this is easy if the substance is an ideal gas (or if some other equation of state can be used, such as the van der Waals equation.)

Example 6.3:

Calculate ΔA for the isothermal expansion of 1.00 mol of an ideal gas from 10.0 L to 25.0 L at 298 K.

Solution:

For an ideal gas,

$$p = \frac{nRT}{V}$$

So

$$\left(\frac{\partial A}{\partial V} \right)_T = -p$$

becomes

$$\left(\frac{\partial A}{\partial V} \right)_T = -\frac{nRT}{V}$$

And so

$$\Delta A = \int_{V_1}^{V_2} \left(\frac{\partial A}{\partial V} \right)_T dV$$

becomes

$$\Delta A = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

or

$$\Delta A = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

Substituting the values from the problem

$$\Delta A = -(1.00 \text{ mol}) \left(8.314 \frac{\text{J}}{\text{mol K}} \right) (298 \text{ K}) \ln \left(\frac{25.0 \text{ L}}{10.0 \text{ L}} \right)$$

$$\Delta A = -2270 \text{ J}$$

But further, it is easy to show that the Maxwell relation that arises from the simplified expression for the total differential of A is

$$\left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$$

This particular Maxwell relation is exceedingly useful since one of the terms, namely $\left(\frac{\partial p}{\partial T} \right)_V$, depends only on p, V, and T. As such it can be expressed in terms of our old friends, α and κ_T !

$$\left(\frac{\partial p}{\partial T} \right)_V = \frac{\alpha}{\kappa_T}$$

Pressure Dependence of G

The pressure and temperature dependence of G is also easy to describe. The best starting place is the definition of G.

$$G = U + pV - TS$$

Taking the differential yields

$$dG = dU + p dV + V dp - T dS - S dT$$

The differential can be simplified by substituting the combined first and second law statement for dU (consider a reversible process and p-V work only).

$$dG = T dS - p dV + p dV + V dp - T dS - S dT$$

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Canceling the Tds and pdV terms leaves

$$dG = Vdp - SdT$$

This suggests that the natural variables of G are p and T . So the total differential dG can also be expressed

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT$$

And by inspection, it is clear that

$$\left(\frac{\partial G}{\partial p}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_p = -S$$

It is also clear that the Maxwell relation on G is given by

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

which is an extraordinarily useful relationship, since one of the terms is expressible entirely in terms of measurable quantities!

$$\left(\frac{\partial V}{\partial T}\right)_p = V\alpha$$

The pressure dependence of G is given by the pressure derivative at constant temperature

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

which is simply the molar volume. For a fairly incompressible substance (such as a liquid or a solid) the molar volume will be essentially constant over a modest pressure range.

Example 6.4:

The density of gold is 19.32 g/cm^3 . Calculate ΔG for a 1.00 g sample of gold when the pressure on it is increased from 1.00 atm to 2.00 atm .

Solution:

The change in the Gibbs function due to an isothermal change in pressure can be expressed as

$$\Delta G = \int_{p_1}^{p_2} \left(\frac{\partial G}{\partial p}\right)_T dp$$

And since $\left(\frac{\partial G}{\partial p}\right)_T = V$, the molar volume

$$\Delta G = \int_{p_1}^{p_2} V dp$$

Assuming that the molar volume is independent of pressure over the stated pressure range, ΔG becomes

$$\Delta G = V(p_2 - p_1)$$

So, the molar change in the Gibbs function can be calculated by substituting the relevant values.

$$\begin{aligned} \Delta G &= \left(\frac{\text{cm}^3}{19.32 \text{ g}} \cdot \frac{197.0 \text{ g}}{\text{mol}} \cdot \frac{\text{L}}{1000 \text{ cm}^3} \right) (2.00 \text{ atm} - 1.00 \text{ atm}) \cdot \frac{8.314 \text{ J}}{0.08206 \text{ atm L}} \\ &= 1.033 \text{ J} \end{aligned}$$

Temperature Dependence of A and G

In differential form, the free energy functions can be expressed as

$$dA = -pdV - SdT \quad \text{and} \quad dG = Vdp - SdT$$

So by inspection, it is easy to see that

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_p = -S$$

And so, it should be fairly straightforward to determine how each changes with changing temperature:

$$\begin{aligned} \Delta A &= \int_{T_1}^{T_2} \left(\frac{\partial A}{\partial T}\right)_V dT = - \int_{T_1}^{T_2} S dT \\ \Delta G &= \int_{T_1}^{T_2} \left(\frac{\partial G}{\partial T}\right)_p dT = - \int_{T_1}^{T_2} S dT \end{aligned}$$

But the temperature dependence of the entropy needed to be known in order to evaluate the integral. A convenient work-around can be obtained starting from the definitions of the free energy functions.

$$A = U - TS \quad \text{and} \quad G = H - TS$$

Dividing by T yields

$$\frac{A}{T} = \frac{U}{T} - S \quad \text{and} \quad \frac{G}{T} = \frac{H}{T} - S$$

Now differentiating each expression with respect to T at constant V or p respectively yields

$$\left(\frac{\partial \left(\frac{A}{T} \right)}{\partial T} \right)_V = -\frac{U}{T^2} \quad \text{and} \quad \left(\frac{\partial \left(\frac{G}{T} \right)}{\partial T} \right)_p = -\frac{H}{T^2}$$

Or differentiating with respect to 1/T provides a simpler form that is mathematically equivalent:

$$\left(\frac{\partial (A/T)}{\partial (1/T)} \right)_V = U \quad \text{and} \quad \left(\frac{\partial (G/T)}{\partial (1/T)} \right)_p = H$$

Focusing on the second expression (since all of the arguments apply to the first as well), we see a system that can be integrated. Multiplying both sides by d(1/T) yields:

$$d\left(\frac{G}{T}\right) = H d\left(\frac{1}{T}\right)$$

Or for finite changes ΔG and ΔH :

$$d\left(\frac{\Delta G}{T}\right) = \Delta H d\left(\frac{1}{T}\right)$$

And integration, assuming the enthalpy change is constant over the temperature interval yields

$$\int_{T_1}^{T_2} d\left(\frac{\Delta G}{T}\right) = \Delta H \int_{T_1}^{T_2} d\left(\frac{1}{T}\right)$$

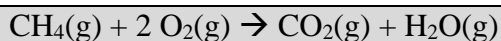
$$\frac{\Delta G_{T_2}}{T_2} - \frac{\Delta G_{T_1}}{T_1} = \Delta H \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

This is the **Gibbs-Helmholtz equation**, and can be used to determine how ΔG changes with changing temperature. The equivalent equation for the Helmholtz function is

$$\frac{\Delta A_{T_2}}{T_2} - \frac{\Delta A_{T_1}}{T_1} = \Delta U \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Example 6.5:

Given the following data at 298 K, calculate ΔG at 500 K for the following reaction:



Compound	ΔG° (kJ/mol)	ΔH° (kJ/mol)
$\text{CH}_4(\text{g})$	-50.5	-74.6
$\text{CO}_2(\text{g})$	-394.4	-393.5
$\text{H}_2\text{O}(\text{g})$	-228.6	-241.8

Solution:

ΔH and $\Delta G_{298 \text{ K}}$ can be calculated fairly easily. It will be assumed that ΔH is constant over the temperature range of 298 K – 500 K.

$$\Delta H = (1 \text{ mol})(-393.5 \text{ kJ/mol}) + (2 \text{ mol})(-241.8 \text{ kJ/mol}) - (1 \text{ mol})(-74.5 \text{ kJ/mol}) = -820.6 \text{ kJ}$$

$$\Delta G_{298} = (1 \text{ mol})(-394.4 \text{ kJ/mol}) + (2 \text{ mol})(-228.6 \text{ kJ/mol}) - (1 \text{ mol})(-50.5 \text{ kJ/mol}) = -801.1 \text{ kJ}$$

So using

$$\frac{\Delta G_{T_2}}{T_2} - \frac{\Delta G_{T_1}}{T_1} = \Delta H \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

With the data just calculated gives

$$\frac{\Delta G_{500}}{500 \text{ K}} - \frac{-801.1 \text{ kJ}}{298 \text{ K}} = (-820.6 \text{ kJ}) \left(\frac{1}{500 \text{ K}} - \frac{1}{298 \text{ K}} \right)$$

$$\Delta G_{500} = -787.9 \text{ kJ}$$

Note: ΔG became a little bit less negative at the higher temperature, which is to be expected for a reaction which is exothermic. An increase in temperature should tend to make the reaction less favorable to the formation of products, which is exactly what is seen in this case!

When Two Variables Change at Once

So far, we have derived a number of expressions and developed methods for evaluating how thermodynamic variables change as one variable changes while holding the rest constant. But real systems are seldom this accommodating. For example, a piece of metal (such as a railroad rail) left in the sun will undergo both an increase in temperature and an expansion due to the absorption of energy from sunlight. So both T and V are changing at the same time! If the change in a thermodynamic variable (such as G) is needed, contributions from both changes are required to be taken into account. We've already seen how to express this in terms of a total differential.

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$$dG = \left(\frac{\partial G}{\partial V}\right)_T dV + \left(\frac{\partial G}{\partial T}\right)_V dT$$

Fortunately, G (like the other thermodynamic functions U , H , S , and A) is kind enough to be a state variable. This means that we can consider the changes independently and then simply add the results. Another way to think of this is that the system may follow either of two pathways to get from the initial conditions to the final conditions:

Pathway 1:

1. An isothermal expansion from V_1 to V_2 at T_1 followed by
2. An isochoric temperature increase from T_1 to T_2 at V_2

Pathway 2:

1. An isochoric temperature increase from T_1 to T_2 at V_1 followed by
2. And isothermal expansion from V_1 to V_2 at T_2

And since G has the good sense to be a state variable, the pathway connecting the initial and final states is unimportant. We are free to choose any path that is convenient to calculate the change.

Example 6.6:

Calculate the entropy change for 1.00 mol of a monatomic ideal gas ($C_V = 3/2 R$) expanding from 10.0 L at 273 K to 22.0 L at 297 K.

Solution:

If one considers entropy to be a function of temperature and volume, one can write the total differential of entropy as

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

and thus

$$\Delta S = \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T}\right)_V dT + \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_T dV$$

The first term is the contribution due to an isochoric temperature change:

$$\begin{aligned} \Delta S_{T_1 \rightarrow T_2} &= \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T}\right)_V dT \\ &= \int_{T_1}^{T_2} \frac{n C_V}{T} dT \end{aligned}$$

$$\begin{aligned}
 &= n C_V \ln \left(\frac{T_2}{T_1} \right) \\
 &= (1.00 \text{ mol}) \left(\frac{3}{2} 8.314 \frac{\text{J}}{\text{mol K}} \right) \ln \left(\frac{297 \text{ K}}{273 \text{ K}} \right) \\
 &= 1.051 \frac{\text{J}}{\text{K}}
 \end{aligned}$$

The second term is the contribution due to an isothermal expansion:

$$\Delta S_{V_1 \rightarrow V_2} = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V} \right)_T dV$$

From the Maxwell relation on A

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$$

So

$$\begin{aligned}
 \Delta S_{V_1 \rightarrow V_2} &= \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial T} \right)_V dV \\
 &= \int_{V_1}^{V_2} \left(\frac{nR}{V} \right) dV \\
 &= n R \ln \left(\frac{V_2}{V_1} \right) \\
 &= (1.00 \text{ mol}) \left(8.314 \frac{\text{J}}{\text{mol K}} \right) \ln \left(\frac{22.0 \text{ L}}{10.0 \text{ L}} \right) \\
 &= 6.56 \frac{\text{J}}{\text{K}}
 \end{aligned}$$

And the total entropy change is

$$\begin{aligned}
 \Delta S_{\text{tot}} &= \Delta S_{T_1 \rightarrow T_2} + \Delta S_{V_1 \rightarrow V_2} \\
 &= 1.051 \frac{\text{J}}{\text{K}} + 6.56 \frac{\text{J}}{\text{K}} \\
 &= 7.61 \frac{\text{J}}{\text{K}}
 \end{aligned}$$

Deriving an expression for a partial derivative.

Partial Derivative Transformation Type III

Thermodynamics involves many variables. But for a single component sample of matter, only two state variables are needed to describe the system and fix all of the thermodynamic properties

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of the system. As such, it is conceivable that two functions can be specified as functions of the same two variables. In general terms:

$$z(x, y) \quad \text{and} \quad w(x, y)$$

So an important question that can be answered is, “What happens to z if w is held constant but x is changed?” To explore this, consider the total differential of z :

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

But z can also be considered a function of x and $w(x, y)$. This implies that the total differential can also be written as

$$dz = \left(\frac{\partial z}{\partial x}\right)_w dx + \left(\frac{\partial z}{\partial w}\right)_x dw$$

And these two total differentials must be equal to one another!

$$\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = \left(\frac{\partial z}{\partial x}\right)_w dx + \left(\frac{\partial z}{\partial w}\right)_x dw$$

If we constrain the system to a change in which w remains constant, the last term will vanish since $dw = 0$.

$$\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = \left(\frac{\partial z}{\partial x}\right)_w dx$$

But also, since w is a function x and y , the total differential for w can be written

$$dw = \left(\frac{\partial w}{\partial x}\right)_y dx + \left(\frac{\partial w}{\partial y}\right)_x dy$$

And it too must be zero for a process in which w is held constant.

$$0 = \left(\frac{\partial w}{\partial x}\right)_y dx + \left(\frac{\partial w}{\partial y}\right)_x dy$$

From this expression, it can be seen that

$$dy = -\left(\frac{\partial w}{\partial x}\right)_y \left(\frac{\partial y}{\partial w}\right)_x dx$$

Substituting this into the previous expression, yields

$$\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left[-\left(\frac{\partial w}{\partial x}\right)_y \left(\frac{\partial y}{\partial w}\right)_x dx\right] = \left(\frac{\partial z}{\partial x}\right)_w dx$$

which simplifies to

$$\left(\frac{\partial z}{\partial x}\right)_y dx - \left(\frac{\partial z}{\partial w}\right)_x \left(\frac{\partial w}{\partial x}\right)_y dx = \left(\frac{\partial z}{\partial x}\right)_w dx$$

So for $dx \neq 0$, implies that

$$\left(\frac{\partial z}{\partial x}\right)_y - \left(\frac{\partial z}{\partial w}\right)_x \left(\frac{\partial w}{\partial x}\right)_y = \left(\frac{\partial z}{\partial x}\right)_w$$

or

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial z}{\partial x}\right)_w + \left(\frac{\partial z}{\partial w}\right)_x \left(\frac{\partial w}{\partial x}\right)_y$$

As with partial derivative transformation types I and II, this result can be achieved in a formal, albeit less mathematically rigorous method.

Consider $z(x, w)$. This allows us to write the total differential for z :

$$dz = \left(\frac{\partial z}{\partial x}\right)_w dx + \left(\frac{\partial z}{\partial w}\right)_x dw$$

Now, divide by dx and constrain to constant y .

$$\left.\frac{dz}{dx}\right|_y = \left(\frac{\partial z}{\partial x}\right)_w \left.\frac{dx}{dx}\right|_y + \left(\frac{\partial z}{\partial w}\right)_x \left.\frac{dw}{dx}\right|_y$$

Noting that $dx/dx = 1$ and converting the other ratios to partial derivatives yields

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial z}{\partial x}\right)_w + \left(\frac{\partial z}{\partial w}\right)_x \left(\frac{\partial w}{\partial x}\right)_y$$

which agrees with the previous result! Again, the method is not mathematically rigorous, but it works so long as w , x , y , and z are state functions, so that the total differentials dw , dx , dy , and dz are exact.

The difference between C_p and C_v

Constant volume and constant pressure heat capacities are very important in the calculation of many changes. The ratio $C_p/C_v = \gamma$ appears in many expressions as well (such as the relationship between pressure and volume along an adiabatic expansion.) It would be useful to derive an expression for the difference $C_p - C_v$ as well. As it turns out, this difference is expressible in terms of measureable physical properties of a substance, such as α , κ_t , p , V , and T .

In order to derive an expression, let's start from the definitions.

$$C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p \quad \text{and} \quad C_v \equiv \left(\frac{\partial U}{\partial T}\right)_v$$

The difference is thus

$$\left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v$$

In order to evaluate this difference, consider the definition of enthalpy:

$$H = U + pV$$

Differentiating this yields

$$dH = dU + p dV + V dp$$

Dividing this expression by dT and constraining to constant p gives

$$\left.\frac{dH}{dT}\right|_p = \left.\frac{dU}{dT}\right|_p + p \left.\frac{dV}{dT}\right|_p + V \left.\frac{dp}{dT}\right|_p$$

The last term is kind enough to vanish (since $dp = 0$ at constant pressure). After converting the remaining terms to partial derivatives:

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p$$

This expression is starting to show some of the players. For example,

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p \quad \text{and} \quad \left(\frac{\partial V}{\partial T}\right)_p = V\alpha$$

So

$$C_p = \left(\frac{\partial U}{\partial T} \right)_p + pV\alpha$$

But what is $\left(\frac{\partial U}{\partial T} \right)_p$? In order to evaluate it, first consider $U(V, T)$. Then the total differential du can be expressed

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

Dividing by dT and constraining to constant p will generate the partial derivative we wish to evaluate:

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

The last term will become unity, so after converting to partial derivatives, we see that

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

(This, incidentally, is an example of partial derivative transformation type III.) Now we are getting somewhere! The last term, $\left(\frac{\partial U}{\partial T} \right)_V$, is C_V . Also, $\left(\frac{\partial V}{\partial T} \right)_p = V\alpha$. So the expression can be rewritten

$$\left(\frac{\partial U}{\partial T} \right)_p = \left(\frac{\partial U}{\partial V} \right)_T V\alpha + C_V$$

If we can find an expression for $\left(\frac{\partial U}{\partial V} \right)_T$ we are almost home free! Fortunately, that is an easy expression to derive. Begin with the combined expression of the first and second laws:

$$dU = TdS - pdV$$

Now, divide both sides by dV and constrain to constant T .

$$\frac{dU}{dV}\bigg|_T = T \frac{dS}{dV}\bigg|_T - p \frac{dV}{dV}\bigg|_T$$

The last term is unity, so after conversion to partial derivatives, we see

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

A Maxwell relation (specifically the Maxwell relation on A) can be used to substitute for $\left(\frac{\partial S}{\partial V}\right)_T$.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

Substituting this into the expression for $\left(\frac{\partial U}{\partial V}\right)_T$ yields

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

And since $\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$,

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{\alpha}{\kappa_T} - p$$

Now, substituting this into the expression for $\left(\frac{\partial U}{\partial T}\right)_p$, we get

$$\begin{aligned} \left(\frac{\partial U}{\partial T}\right)_p &= \left[T \frac{\alpha}{\kappa_T} - p \right] V \alpha + C_V \\ &= \frac{TV\alpha^2}{\kappa_T} - pV\alpha + C_V \end{aligned}$$

This can now be substituted into the expression

$$C_p = \left(\frac{\partial U}{\partial T}\right)_p + pV\alpha$$

yields

$$C_p = \frac{TV\alpha^2}{\kappa_T} - pV\alpha + C_V + pV\alpha$$

The $pV\alpha$ terms will cancel. And subtracting C_V from both sides gives the desired result:

$$C_p - C_v = \frac{TV\alpha^2}{\kappa_T}$$

And this is a completely general result since the only assumptions made were those that allowed us to use the combined first and second laws in the form $dU = TdS - pdV$. That means that this expression can be applied to any substance whether gas, liquid, animal, vegetable, or mineral. But what is the result for an ideal gas?

Since we know that for an ideal gas

$$\alpha = \frac{1}{T} \quad \text{and} \quad \kappa_T = \frac{1}{p}$$

Substitution yields

$$\begin{aligned} C_p - C_v &= \frac{TV \left(\frac{1}{T}\right)^2}{\left(\frac{1}{p}\right)} \\ &= \frac{pV}{T} \\ &= R \end{aligned}$$

So for an ideal gas, $C_p - C_v = R$. That is good to know, no?

Example 6.7:

Derive the expression for the difference between C_p and C_v by beginning with the definition of H , differentiating, dividing by dV (to generate the partial derivative definition of C_v). In this approach, you will need to find expressions for $\left(\frac{\partial H}{\partial T}\right)_V$, and $\left(\frac{\partial U}{\partial p}\right)_T$, and also utilize the Maxwell-Relation on G .

Solution:

Begin with the definition of enthalpy.

$$H = U + pV$$

Differentiate the expression.

$$dH = dU + pdV + Vdp$$

Now, divide by dV and constrain to constant T (as described in the instructions) to generate the partial derivative definition of C_v .

$$\left. \frac{dH}{dT} \right|_V = \left. \frac{dU}{dT} \right|_V + p \left. \frac{dV}{dT} \right|_V + V \left. \frac{dp}{dT} \right|_V$$

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

Now what is needed is an expression for $\left(\frac{\partial H}{\partial T} \right)_V$. This can be derived from the total differential for H(p,T) by dividing by dT and constraining to constant V.

$$dH = \left(\frac{\partial H}{\partial p} \right)_T dp + \left(\frac{\partial H}{\partial T} \right)_p dT$$

$$\left. \frac{dH}{dT} \right|_V = \left(\frac{\partial H}{\partial p} \right)_T \left. \frac{dp}{dT} \right|_V + \left(\frac{\partial H}{\partial T} \right)_p \left. \frac{dT}{dT} \right|_V$$

$$\left(\frac{\partial H}{\partial T} \right)_V = \left(\frac{\partial H}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_V + \left(\frac{\partial H}{\partial T} \right)_p$$

This again is an example of **Partial Differential Transformation Type III**. To continue, we need an expression for $\left(\frac{\partial H}{\partial p} \right)_T$. This can be quickly generated by considering the total differential of H(p,S), its natural variables:

$$dH = TdS + Vdp$$

Dividing by dp and constraining to constant T yields

$$\left. \frac{dH}{dp} \right|_T = T \left. \frac{dS}{dp} \right|_T + V \left. \frac{dp}{dp} \right|_T$$

$$\left(\frac{\partial H}{\partial p} \right)_T = T \left(\frac{\partial S}{\partial p} \right)_T + V$$

Using the Maxwell Relation on G, we can substitute

$$-\left(\frac{\partial V}{\partial T} \right)_p = \left(\frac{\partial S}{\partial p} \right)_T$$

So

$$\left(\frac{\partial H}{\partial p} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_p + V$$

Now, substitute this back into the expression for $\left(\frac{\partial H}{\partial T}\right)_V$

$$\left(\frac{\partial H}{\partial T}\right)_V = \left[-T\left(\frac{\partial V}{\partial T}\right)_p + V\right]\left(\frac{\partial p}{\partial T}\right)_V + \left(\frac{\partial H}{\partial T}\right)_p$$

$$\left(\frac{\partial H}{\partial T}\right)_V = -T\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial p}{\partial T}\right)_V + V\left(\frac{\partial p}{\partial T}\right)_V + \left(\frac{\partial H}{\partial T}\right)_p$$

This can now substituted for the right-hand side of the initial expression for $\left(\frac{\partial H}{\partial T}\right)_V$:

$$-T\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial p}{\partial T}\right)_V + V\left(\frac{\partial p}{\partial T}\right)_V + \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + V\left(\frac{\partial p}{\partial T}\right)_V$$

The $V\left(\frac{\partial p}{\partial T}\right)_V$ terms are kind enough to cancel one another. The expression can then be rearranged to yield

$$\left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial p}{\partial T}\right)_V$$

Or

$$C_p - C_V = \frac{TV\alpha^2}{\kappa_T}$$

which might look familiar!

Vocabulary and Concepts

free energy	134	maximum work	135
Gibbs Free Energy	128	Maxwell Relation.....	132
Gibbs function.....	128	standard free energy of formation (ΔG_f°)	129
Gibbs-Helmholtz equation.....	141		
Helmholtz function	129		

Learning Objectives

After mastering the material presented in this chapter, one will be able to:

1. Define the free energy functions A and G, and relate changes in these functions to the spontaneity of a given process and constant volume and pressure respectively.
2. Use the definitions of entropy and reversible work of expansion to write an equation that combines the first and second laws of thermodynamics.
3. Utilize the combined first and second law relationship to derive Maxwell Relations stemming from the definitions of U, H, A, and G.
4. Utilize the Maxwell Relations to derive expressions that govern changes in thermodynamic variable as systems move along specified pathways (such as constant temperature, pressure, volume, or adiabatic pathways.)
5. Derive and utilize an expression describing the volume dependence of A.
6. Derive and utilize an expression describing the pressure dependence of G.
7. Derive and utilize expressions that describe the temperature, dependence of A and G.
8. Derive an expression for, and evaluate the difference between C_p and C_v for any substance, in terms of T, V, α , and κ_T .

Problems

1. Using data found at http://chem.libretexts.org/Reference/Reference_Tables/Thermodynamics_Tables/T1%3A_Standard_Thermodynamic_Quantities, calculate the standard reaction Gibbs functions (ΔG°) for the following reactions at 298 K.
 - a. $\text{CH}_3\text{CH}_2\text{OH}(\text{l}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{l})$
 - b. $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6 \text{O}_2 \rightarrow 6 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{l})$
 - c. $2 \text{POCl}_3(\text{l}) \rightarrow 2 \text{PCl}_3(\text{l}) + \text{O}_2(\text{g})$
 - d. $2 \text{KBr}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{KCl}(\text{s}) + \text{Br}_2(\text{l})$
 - e. $\text{SiH}_4(\text{g}) + 2 \text{Cl}(\text{g}) \rightarrow \text{SiCl}_4(\text{l}) + 2 \text{H}_2(\text{g})$
2. Estimate ΔG at 1000 K from its value at 298 K for the reaction
$$\text{C}(\text{s}) + 2 \text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) \quad \Delta G = -50.75 \text{ kJ at } 298 \text{ K}$$
3. The standard Gibbs function for formation (ΔG_f°) of $\text{PbO}_2(\text{s})$ is -217.4 kJ/mol at 298 K. Assuming O_2 is an ideal gas, find the standard Helmholtz function for formation (ΔA_f°) for PbO_2 at 298K.
4. Calculate the entropy change for 1.00 mol of an ideal monatomic gas ($C_v = 3/2 R$) undergoing an expansion and simultaneous temperature increase from 10.0 L at 298 K to 205.0 L at 455 K.

5. Consider a gas that obeys the equation of state

$$p = \frac{nRT}{V - nb}$$

- a. Find expressions for α and κ_T for this gas.
 - b. Evaluate the difference between C_p and C_v for the gas.
6. Show that $\left(\frac{\partial C_p}{\partial p}\right)_T = 0$ for an ideal gas.

7. Derive the thermodynamic equation of state

$$\left(\frac{\partial H}{\partial p}\right)_T = V(1 - T\alpha)$$

8. Derive the thermodynamic equation of state

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{\alpha}{\kappa_T} - p$$

9. The “Joule Coefficient” is defined by

$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U$$

Show that

$$\mu_J = \frac{1}{C_V} \left(p - \frac{T\alpha}{\kappa_T} \right)$$

and evaluate the expression for an ideal gas.

10. Derive expressions for the pressure derivatives $\left(\frac{\partial X}{\partial p}\right)_T$ of U, H, A, G, and S at constant temperature in terms of measurable properties. (The derivation of $\left(\frac{\partial H}{\partial p}\right)_T$ was done in problem 7.) Evaluate the expressions for $\left(\frac{\partial S}{\partial p}\right)_T$, $\left(\frac{\partial H}{\partial p}\right)_T$, and $\left(\frac{\partial U}{\partial p}\right)_T$ for a van der Waals gas.

11. Derive expressions for the volume derivatives $\left(\frac{\partial X}{\partial V}\right)_T$ of U, H, A, G, and S at constant temperature in terms of measurable properties. (The derivation of $\left(\frac{\partial U}{\partial V}\right)_T$ was done in problem 8.) Evaluate the expressions for $\left(\frac{\partial X}{\partial V}\right)_T$ and $\left(\frac{\partial X}{\partial V}\right)_T$ for a van der Waals gas.
12. Evaluate the difference between C_p and C_v for a gas that obeys the equation of state

$$p = \frac{nRT}{V - nb}$$

13. The adiabatic compressibility (κ_S) is defined by

$$\kappa_S \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S$$

Show that for an ideal gas,

$$\kappa_S = \frac{1}{p\gamma}$$