

Ideal Gas Model --- Calculating Δu and Δh (The BIG picture!)

The ideal gas model is used to predict the behavior of gases and is one of the most useful and commonly used substance models ever developed. Its use is ubiquitous in introductory chemistry and physics courses; however, one must always remember that it is only a model. And as with any model, it is only valid under certain conditions.

The purpose of this brief note is to clarify a limitation inherent in the form of the ideal model presented in ES201 — the ideal gas model with constant, room-temperature specific heats. We will first review the model and then see how assuming constant, room-temperature specific heats limits the accuracy of our calculations.

Ideal Gas Model with Room-Temperature Specific Heats

As presented in this course, the ideal gas model is based on three key assumptions:

- (1) The pressure, volume, and temperature of an ideal gas obey the following equation¹:

$$PV = NR_u T \quad \text{or} \quad PV = mRT \quad \text{where} \quad R = \frac{R_u}{M}$$

- (2) The specific internal energy only depends on temperature:

$$u = u(T)$$

- (3) The molar mass of an ideal gas is identical with the molar mass of the real substance:

$$M_{\text{ideal gas}} = M_{\text{real substance}}$$

To further simplify the calculations, we make one more assumption:

- (4) The specific heats — c_p and c_v — are independent of temperature which means that they are constants. Furthermore, when numerical values are required for computations, we use the values measured at room temperature.

When all four assumptions are invoked, we say that we are modeling a gas as an **ideal gas with room-temperature specific heats**. This is the form of the ideal gas model we will use in ES201 for *all* calculations involving an ideal gas.

Assumption (4) simplifies many calculations; however, the specific heats are functions of temperature. Assuming them to be constants may under certain conditions lead to significant errors in calculating changes in specific internal energy u , specific enthalpy h , and specific entropy s . (Entropy will be introduced in Chapter 8.) In the following section, we will explore this error.

¹ Although we have stated three assumptions here, only the first assumption -- $PV = NR_u T$ -- is necessary and sufficient to predict the behavior of an ideal gas. The other assumptions are listed here to emphasize important consequences of the first assumption that cannot be easily proven without further study of thermodynamics or physical chemistry.

How Bad is Assuming Constant, Room-Temperature Specific Heats

We will first consider how this assumption influences how we calculate a change in specific internal energy, Δu .

By definition, the **specific heat at constant volume** c_v is defined for *all* substances as the partial derivative of specific internal energy u with respect to temperature T with specific volume v held constant:

$$c_v = \left(\frac{\partial u}{\partial T} \right)_v$$

For an ideal gas, it can be shown (or assumed as in assumption 3 above) that the specific internal energy u is only a function of temperature: $u = u(T)$. Combining this assumption with the definition for c_v , we get an equation for the differential change in the specific internal energy of an ideal gas:

$$c_v = \left(\frac{\partial u}{\partial T} \right)_v = \left[\frac{\partial}{\partial T} (u_{(T)}) \right]_v = \frac{du}{dT} \quad \Rightarrow \quad \boxed{du = c_v dT}$$

where c_v is only a function of temperature T . Figure 1 shows the specific heat at constant volume c_v as function of temperature for two gases, air and carbon dioxide. Table 1 provides numerical values for c_v for four gases over a temperatures.

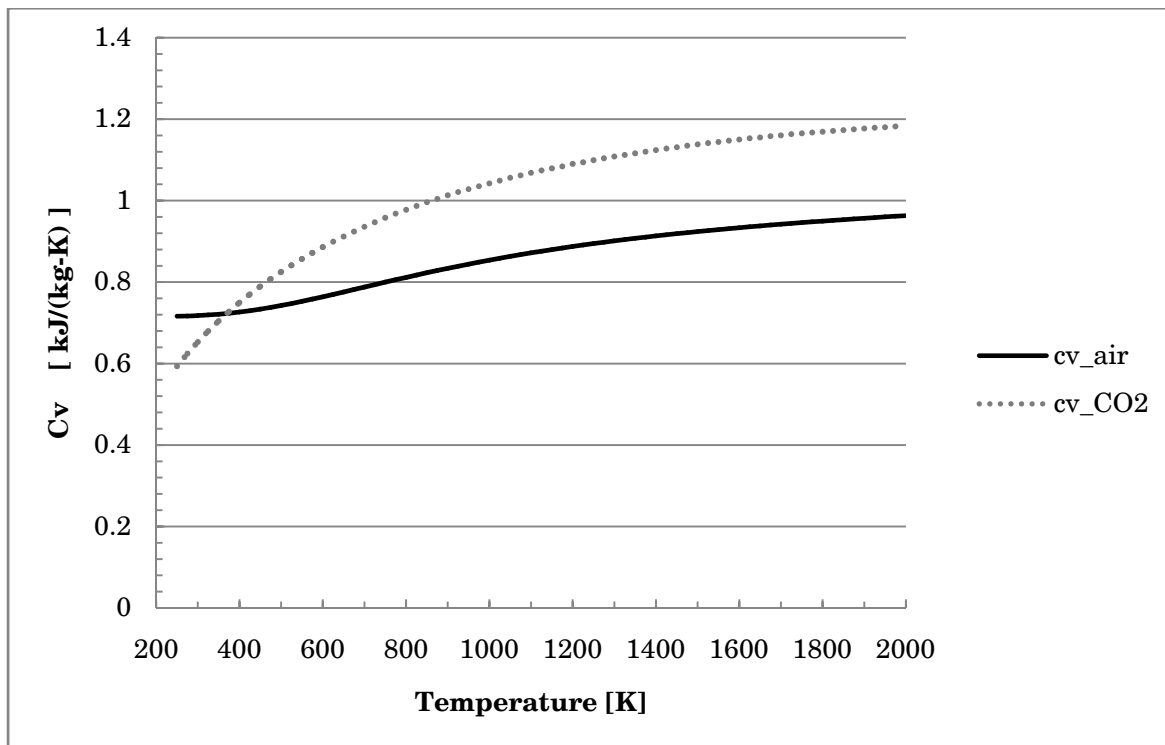


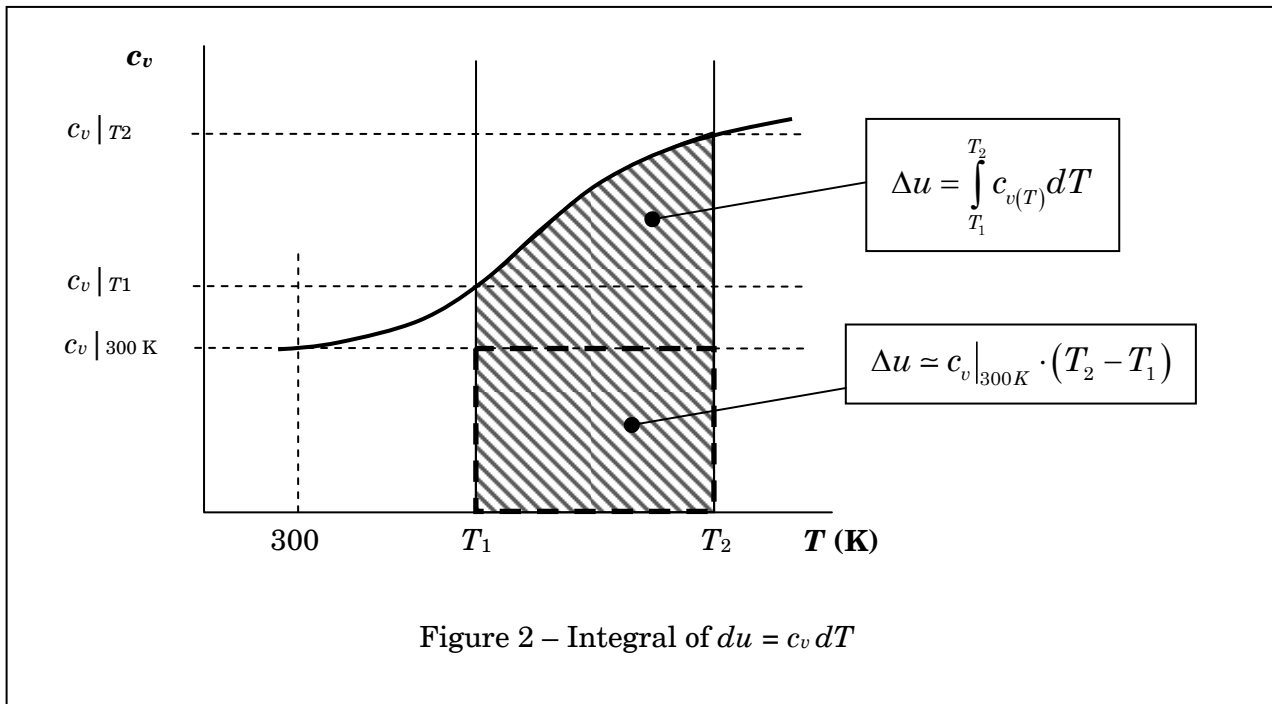
Figure 1 – Variation of ideal gas specific heat with temperature

Table 1 — Ideal Gas Constant-Volume Specific Heat				
c_v [kJ/(kg-K)]				
T (K)	Air	O ₂	CO	CO ₂
300	0.7177	0.6618	0.7445	0.6529
400	0.7262	0.6801	0.7478	0.7494
500	0.7423	0.7140	0.7694	0.8249
600	0.7638	0.7451	0.7952	0.8857
700	0.7876	0.7713	0.8207	0.9358
800	0.8114	0.7932	0.8445	0.9775
900	0.8337	0.8116	0.8662	1.013
1000	0.8538	0.8274	0.8858	1.042

While the specific heats are of interest in their own right, our real goal is to evaluate Δu , the change in specific internal energy. To do this we integrate the differential change in the specific internal energy as follows:

$$\Delta u = u_2 - u_1 = \int_{T_1}^{T_2} du = \int_{T_1}^{T_2} c_v dT$$

From calculus we know that any integral represents an area under a curve. Looking at Figure 2, we see that this integral is really just the area under the c_v vs. T curve (the cross-hatched area). To accurately evaluate the change in specific internal energy between T_1 and T_2 , we must know how c_v depends on temperature. This information is typically available as an equation, as a graph (Figure 1), or as a set of discrete values such as shown in Table 1.



By assuming constant specific heats evaluated at room temperature (300K), we calculate the change in specific internal energy as follows:

$$\Delta u = \int_{T_1}^{T_2} c_{v(T)} dT \approx c_{v(300\text{ K})} (T_2 - T_1)$$

Referring back to Figure 2, we see that this integral is just the area inside the rectangular box outlined by a dark dashed line. The difference between the cross-hatched area and the dashed-line box area represents the error in using this approximation.

If c_v was constant, then this approximation would introduce no error. (The specific heats of monatomic gases like argon, helium, and neon are relative insensitive to temperature.) However, because c_v changes with temperature for most gases, we need to investigate the error. Examining Figure 1, we can see that assuming constant c_v appears to be a good assumption for air near 300K but a poor assumption for carbon dioxide. Table 2 shows the maximum error we in calculating Δu if we assume constant, room-temperature values for c_v . As one might expect, the farther you move away from room temperature (300 K) the larger the error.

T (K)	% Error = $[\Delta u_{\text{room}} - \Delta u_{\text{actual}}] / \Delta u_{\text{actual}}$			
	Air	O ₂	CO	CO ₂
300	0.0	0.0	0.0	0.0
400	-1.2	-2.7	-0.4	-12.9
500	-3.3	-7.3	-3.2	-20.9
600	-6.0	-11.2	-6.4	-26.3
700	-8.9	-14.2	-9.3	-30.2
800	-11.5	-16.6	-11.8	-33.2
900	-13.9	-18.5	-14.0	-35.5
1000	-15.9	-20.0	-16.0	-37.3

Errors of similar magnitude would also be found in calculating a change in specific enthalpy Δh or a change in specific entropy Δs .

Thus our model — the ideal gas with room-temperature specific heats — will only accurately calculate Δu , Δh , and Δs at temperatures near room temperature. If for instance we were to use this model to find out how much work is done by the piston in your car engine during the compression stroke our model could significantly underestimate the work required. However, this is a limitation we are willing to accept this quarter so that we can learn to use substance models in our energy and entropy calculations. Next quarter in ES202 – Fluid & Thermal Systems we will relax this restriction and learn how to more accurately calculate Δu , Δh , and Δs for an ideal gas at any temperature.