

A Review and Evaluation of Specific Heat Capacities of Rocks, Minerals, and Subsurface Fluids. Part 2: Fluids and Porous Rocks

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Heat capacities of solid sediments and pore fluids within a basin can influence geothermal gradients when sedimentation or erosion is rapid. This paper provides data on specific heat capacities of pore fluids and porous rocks. It includes data on specific heat capacities of water, ice, and gas hydrates at reference temperatures, as well as equations for calculating the specific heat capacity of those substances as a function of temperature. It also provides values for specific heat capacities of oil and natural gases at low temperatures, as well as equations describing the temperature and pressure dependence of the specific heat capacities of those substances. Finally, it shows how to calculate the specific heat capacity of mixtures of solid materials, or of mixtures of solids and pore fluids. The data and equations provided herein can be incorporated directly into existing modeling software by users and software developers.

KEY WORDS: Basin modeling, thermal capacity, specific heat capacity.

INTRODUCTION

This paper focuses on the specific heat capacities of pore fluids (water, ice, oil, and gas), and of porous rocks containing one or more of these fluids. Specific heat capacities will be specified at a standard reference temperature of 20°C, and as a function of temperature. Pressure effects on fluids also will be considered. A companion paper (Waples and Waples, 2004) discusses heat capacity as a physical phenomenon, as well as the specific heat capacities and thermal capacities of minerals and nonporous rocks. The reader is referred to that paper for definitions and data on solid materials, as well as for examples of the importance of heat capacity in basin modeling.

The heat capacity of any substance is the amount of heat required to raise the temperature of that substance by one degree (usually Celsius or Kelvin, which are equivalent in this calculation). The specific heat

capacity (also simply specific heat) of a substance is the heat capacity per unit mass of that substance. Here we shall discuss specific heat capacity using SI units (J/kg/K). These units can be converted to cal/g/°C by dividing by 1000 and then dividing again by 4.184. Specific heat capacity also is expressed in heat units per mole, especially for gases. This conversion can be performed by multiplying by the molecular weight, divided by 1000, to get J/mol/K. The specific heat capacity per unit volume of substance, termed thermal capacity, is obtained by multiplying the specific heat capacity by the density:

$$\text{Thermal capacity} = (\text{Specific heat capacity}) * (\text{Density}) \quad (1)$$

Thermal capacity is expressed in units of J/cm³/K.

Heat capacity can be expressed at constant volume (Cv) or constant pressure (Cp). In this paper we will use Cp.

OBJECTIVE

The objectives of this paper are to provide: (1) values of specific heat capacities for geological fluids

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for ranges of temperatures typically expected in sedimentary basins; (2) equations for calculating specific heat capacities of mixtures of fluids and solids; and (3) equations for taking pressure effects into account, if appropriate. The ultimate objective of providing these heat capacities and reviewing existing equations is to derive a small set of equations that can be used easily and conveniently by model users and developers to include better the effects of temperature and pressure in modeling software.

FLUIDS

This paper considers four types of fluids: liquid water, ice, oil, and natural gas. Existing maturity-modeling and basin-modeling software programs normally assume that liquid water is the only pore fluid present, but values and equations presented here will allow software developers to begin to include a variety of fluids.

Water

The specific heat capacity of water is well known for a wide range of temperatures. Using data from Holman (1958), Somerton (1992) developed equations for the specific heat capacity of pure water as a function of temperature ($^{\circ}\text{C}$). For temperatures between 20°C and 290°C , specific heat capacity is given by:

$$C_p(\text{J/kg/K}) = (4245 - 1.841T)/\rho_w \quad (2)$$

Equation (2) probably can be extrapolated down to 0°C without significant error, and thus can be used for most sediments and sedimentary rocks. At temperatures between 290°C and 373°C Somerton (1992) proposed:

$$C_p(\text{J/kg/K}) = (3703/\rho_w) * \exp -[0.00481 * (T-290) + 0.000234 * (T-290)^2] \quad (3)$$

Water contents of rocks at temperatures above 373°C are negligible, so additional equations are not necessary. Specific heat capacity of pure water calculated using Equations (2) and (3) is plotted as a function of temperature in Figure 1.

The density ρ_w of liquid water in Equations (2) and (3) was expressed by Holman (1958, cited by Somerton, 1992) as

$$\rho_w = \rho_{w20}/[1 + (T - 20)\beta_w] \quad (4)$$

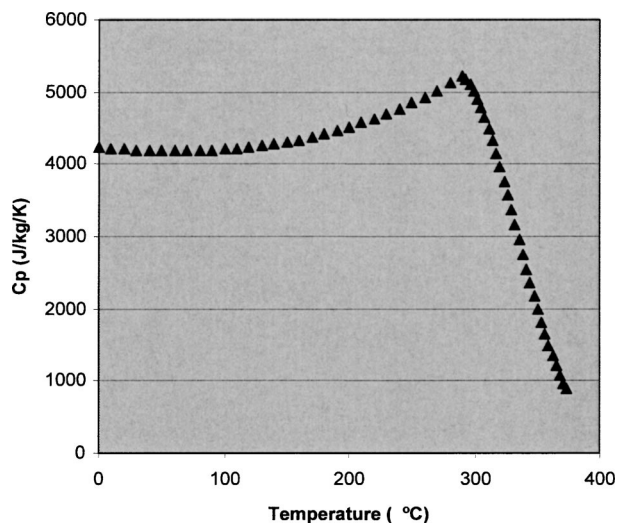


Figure 1. Specific heat capacity of water as function of temperature from 0°C to 373°C , calculated using Equations (2) and (3).

where T is the temperature in $^{\circ}\text{C}$, ρ_{w20} is the density of water at 20°C , and β_w is the coefficient of thermal expansion of water, given by

$$\beta_w = 0.0002115 + 1.32 * 10^{-6}T + 1.09 * 10^{-8}T^2 \quad (5)$$

The data shown in Figure 1 and the values used in the development of Equations (4) and (5) were obtained at the high pressures necessary to maintain water in its liquid state. The specific heat capacity for liquid water is only slightly sensitive to changes in pressure that are independent of changes in temperature. For example, Somerton (1992) reported that at 27°C the specific heat capacity for water at 20.7 MPa is only 2.5% less than that at atmospheric pressure. Therefore, as long as the pressure is high enough to keep the water in a liquid phase, the specific heat capacity of water under subsurface (high pressure) conditions can be estimated with good accuracy using Equations (2)–(5), without including pressure dependence.

If the pore water is saline, the appropriate value for ρ_{w20} of water of that particular salinity can be used in Equation (4). According to Kobranova (1989), the specific heat capacity of saline water is slightly lower than that of pure water. Because the difference is too small to be of significance in modeling, waters of all salinities will be assumed here to have the same specific heat capacity.

Similar to specific heat, the thermal capacity of liquid water is high relative to other minerals and fluids. For example, at a temperature of 100°C , with a density of 0.965 g/cm^3 [Eq. (4)] and a specific heat

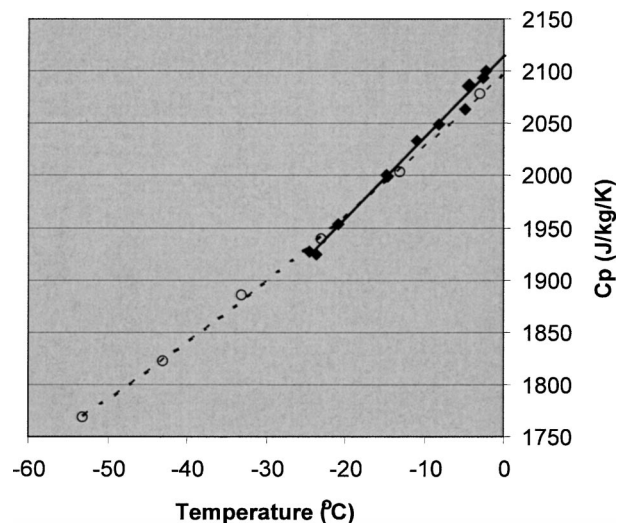


Figure 2. Specific heat capacity of ice (solid diamonds) and methane hydrate (open circles) as function of temperature. Ice data from Weast and Selby (1967); methane hydrate data from Sloan (1990). Lines represent best least-squares fits: solid line is for ice, whereas dashed line is for methane hydrate. Equation (6) describes ice, and Equation (12) describes methane hydrate.

capacity of 4208 J/kg/K [Eq. (2)], the thermal capacity of pure water is 4.06 J/cm³/K.

Ice

The specific heat capacity and thermal capacity of ice are about half those of liquid oil (see next). Figure 2 shows the trend of measured specific heat capacity of ice as a function of temperature between -25°C and 0°C. The trend can be described by Equation (6), where T is in °C:

$$C_p(\text{J/kg/K}) = 7.8277T + 2115 \quad (6)$$

Oil

Gambill (1957) presented three equations for calculating the specific heat capacity of oil as a function of temperature (T) and the specific gravity of the oil (S). In each situation the temperature is expressed in °C and specific heat capacity in J/kg/K.

$$C_p = (1684 + 3.389T)/S^{0.5} \quad (7)$$

$$C_p = 2.061 * (2.1 - S) * (1.8T + 702) \quad (8)$$

$$C_p = 2092S^{0.5} + 2.9297T - 43.7 \quad (9)$$

According to Standing (1977, cited in Somerton, 1992) the density of oil at any temperature can be calcu-

lated using Equation (4). This equation is the same as that used for calculating water density, except that the density of oil at 20°C (ρ_{o20}) is substituted for ρ_{w20} , and the coefficient of thermal expansion of oil, β_o , is substituted for that of water, β_w is calculated using Equation (10):

$$\beta_o = 0.000442 + 0.0000103 * \text{API} \quad (10)$$

where API is the API gravity, equal to $141.5/\rho_{o20} - 131.5$.

Equations (7)–(9) are valid between about 0°C and 200°C, and are accurate to within 2% to 5% (Gambill, 1957); Equations (7) and (8) are valid for the complete range of densities of oils, whereas the valid density range for Equation (9) was not specified. It is not clear which, if any, equation would be appropriate at temperatures above 200°C, because they are all valid only to about 200°C (Gambill, 1957). However, because on a geologic time scale oil generally is unstable at temperatures above 200°C (Waples, 2000), the question is moot.

Figure 3 shows a comparison of the three equations at temperatures within the calibrated range, assuming two different oil gravities. For an oil of density 0.9 g/cm³ (25° API), all three equations give similar results. For a light oil (density = 0.8 g/cm³ = 45° API), however, the three equations make rather different predictions. Of the three, Equation (7) shows the least variation with changes in API gravity. Somerton (1992) also selected this equation among the three offered by Gambill (1957), although he did not justify his choice. Somerton's adaptation of Gambill's equation has an error in it, however.

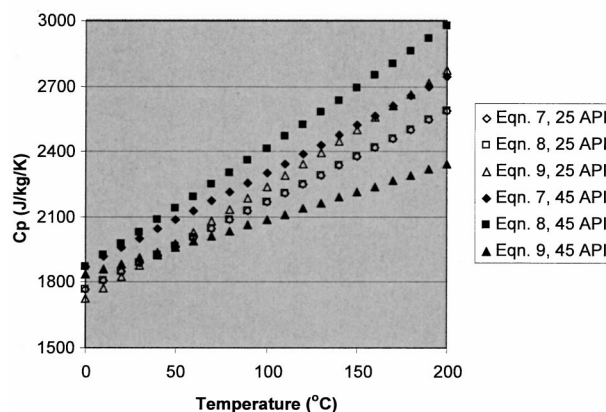


Figure 3. Specific heat capacities of two oils (25° API, 45° API) calculated using Equations (7), (8), and (9). Oil density as function of temperature was calculated using equation of Standing (1977, cited in Somerton, 1992).

The specific heat capacity of oil at room temperature obtained from Equations (7)–(9) is about 1800 J/kg/K. This value is slightly less than that of ice (compare Fig. 3 with Fig. 2), and slightly less than half the value of liquid water.

Gases

Somerton (1992) commented that the contribution of gases to sedimentary heat capacity is so small that it can be neglected. Although this statement is fundamentally valid, it is of interest or importance to include gases in the heat-capacity calculation.

The specific heat capacity of methane generally increases with increasing temperature and increasing pressure (Somerton, 1992). Spencer (1945) described the temperature dependence of the specific heat capacity of gases using second- and third-order polynomials. Alternatively, the temperature dependence of the specific heat capacity of methane reported by Somerton (1992) can be described using fourth-order polynomials:

$$C_p = AT^4 + BT^3 + CT^2 + DT + E \quad (11)$$

Figure 4 shows the specific heat capacity of methane at four different pressures. It is clear that pressure exerts an important control on the specific heat capacity of methane. In order to simplify inclusion of pressure in the heat-capacity calculation, each of the coefficients in Equation (11) was expressed as a fourth-order polynomial. Table 1 shows the values of the coefficients A, B, C, D, and E in Equation (11) expressed as functions of pressure P. For example, the value of A

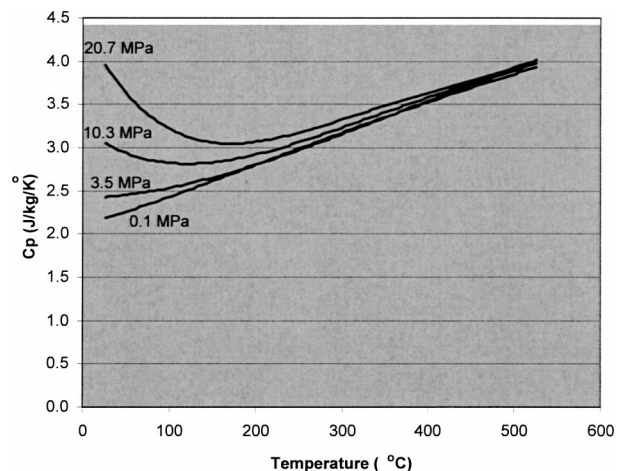


Figure 4. Specific heat capacity of methane as function of temperature at four different pressures. Data from Somerton (1992).

is given by $2.031 \times 10^{-7}P^4 + 5.702 \times 10^{-5}P^3 - 5.175 \times 10^{-3}P^2 + 0.1315P - 0.1813$, where P is in MPa. This approach is fundamentally the same as that adopted by Richardson (1992) in describing thermal conductivities of coals as a function of coal rank.

Figure 5 shows the calculated profile of the specific heat capacity of methane as a function of depth in a section where the geothermal gradient is 30°C/km and pressure is hydrostatic. If the geothermal gradient is higher, or if the section is overpressured, the specific heat capacity of the methane at any given depth would be a bit higher. However, the difference will be slight, and can be ignored.

Given the minor fraction of gas in the total pore fluids in any sedimentary section, and the relative constancy of the specific heat capacity of methane below a depth of about 1500 m, it is completely satisfactory to use a constant value for the specific heat capacity of natural gas. The mean value for the 8000 m section shown in Figure 5 is about 3250 J/kg/K.

Although the specific heat capacity of methane is higher than that of any material we have considered except liquid water, its thermal capacity is lower because the thermal capacity depends on density. Gas density is highly dependent on pressure and somewhat dependent on temperature. For example, the density of methane drops by about a factor of three as temperature increases from room temperature to 500°C (Somerton, 1992). In going from atmospheric pressure to 20 MPa, in contrast, it increases by about a factor of 200 (Somerton, 1992). At a density of about 0.15 g/cm³ (typical of many gas reservoirs) and a pressure of 25 MPa (representing normal pressure at about 2500 m), the specific heat capacity of methane should be about 3300 J/kg/K and the thermal capacity consequently is equal to 0.5 J/cm³/K. However, a gas under high pressure might have a density (0.6 g/cm³) approaching that of light oil, and consequently a thermal capacity similar to that of oil.

The specific heat capacities of other gas components, such as ethane, carbon dioxide, and nitrogen, are 25% to 60% lower than that of methane (Gordon and Ford, 1972). However, because in most situations their contribution to the total gases present will be small compared to that of methane, the data for methane can be used for most subsurface gases.

Gas hydrates

Gas hydrates are clathrates, in which a single molecule of gas is trapped inside a cage network of

Table 1. Coefficients of Fourth-order Polynomials Describing Each of Constants A-E in Equation (11) in Terms of Pressure P (MPa). Derived from Data Taken from Somerton (1992). See Text for Discussion.

Coefficient in Equation (11)	Coefficient of P ⁴	Coefficient of P ³	Coefficient of P ²	Coefficient of P ¹	Coefficient of P ⁰
A	-2.03E-07	5.70E-05	-0.00518	0.132	-0.181
B	2.84E-07	-7.88E-05	0.00714	-0.188	0.207
C	-1.42E-06	3.88E-04	-0.03513	0.980	-0.872
D	2.95E-07	-7.97E-05	0.00725	-0.222	0.533
E	-2.00E-07	5.46E-05	-0.00519	0.193	1.928

water molecules. They may occur in areas with permafrost, as well as in deep-water marine sediments. The formula for methane hydrate is CH₄·6H₂O; that for ethane hydrate is C₂H₆·7.67H₂O; and that for propane hydrate is C₃H₈·17H₂O (Sloan, 1990). Table 2 shows that specific heat capacities of all three hydrates are similar for a geologically relevant range of temperatures.

Figure 2 demonstrates that the specific heat capacity of methane hydrate is virtually the same as that of ice. Thus it is not necessary to distinguish between ordinary ice and gas hydrate for modeling purposes, nor is it necessary to estimate or establish the composition of the gas hydrate. If desired, however, the specific heat capacity of methane hydrate (C_{pmh}, in J/kg/K) at any temperature T (°C) can be well described by Equation (12), which was fit to the ice data from Weast and Selby (1967) and the methane hydrate

data from Sloan (1990):

$$C_{pmh} = 0.0199T^2 + 7.235T + 2097 \quad (12)$$

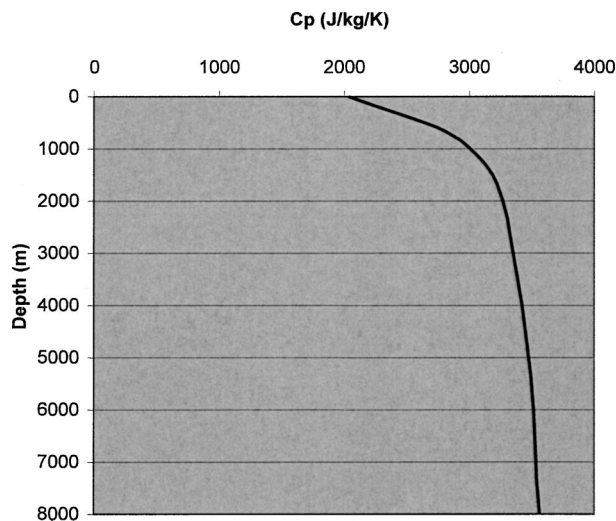
Summary

Figure 6 compares the specific heat capacities of water, oil, and gas in a typical geologic section in which the surface temperature is 20°C and the geothermal gradient is 30°C/km.

The specific heat capacity of oil is about half that of water, whereas that of methane is intermediate between those of oil and water. Specific heat capacities of oil and gas increase with increasing temperature, while that of water is practically constant from 20°C to about 120°C. At higher temperatures it too rises, until it begins to decrease when the temperature exceeds 290°C.

POROUS ROCKS

The thermal capacity of a real rock (that is, a mixture of solids and liquids) normally is calculated as the weighted average of the thermal capacities of the various solids and liquids (Gambill, 1957; Buntebarth, 1984; Kobranova, 1989; Somerton, 1992; Scharli and Rybach, 2001). The specific heat capacity of the rock then can be calculated by dividing the thermal capac-

**Figure 5.** Specific heat capacity of methane as function of depth at hydrostatic pressure assuming geothermal gradient of 30°C/km. Calculation was carried out using Equation (11) and constants given in Table 1.**Table 2.** Specific Heat Capacities of Methane, Ethane, and Propane Hydrates as Function of Temperature. Data from Sloan (1990).

T (°C)	Methane (J/kg/K)	Ethane (J/kg/K)	Propane (J/kg/K)
-53	1769	1742	1713
-43	1822	1795	1765
-33	1885	1850	1840
-23	1939	1922	1927
-13	2003	2010	2029
-3	2077		

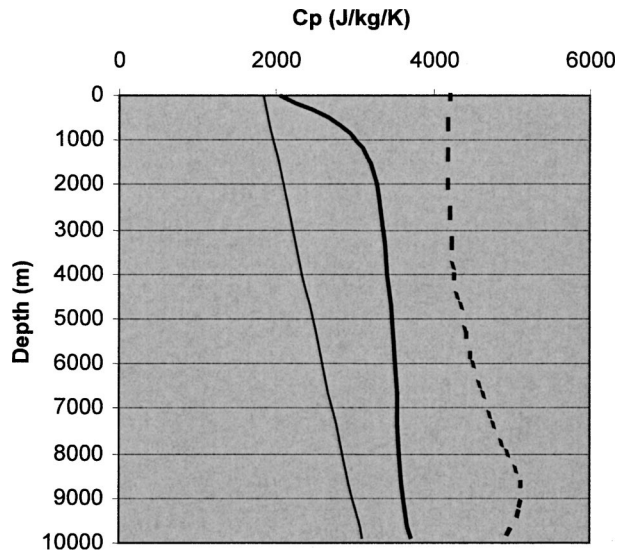


Figure 6. Calculated specific heat capacities of oil (thin solid line), methane (heavy solid line), and water (heavy dashed line) plotted as function of depth, assuming surface temperature of 20°C and geothermal gradient of 30°C/km. Specific heat capacities of oil were calculated using Equation (7), assuming that oil is 25° API gravity (density = 0.9 g/cm³ at 20°C). Those of methane were calculated using Equation (11), whereas those of water were calculated using Equations (2) and (3).

ity by the density of the rock, including pore fluids. As an example, the specific heat capacity Cp_{rock} for a rock containing water or ice as its only pore fluid is given by

$$Cp_{rock} = [\rho_{solid} * Cp_{solid} * (1 - \phi) + \rho_{H2O} * Cp_{H2O} * \phi] / \rho_{rock} \quad (13)$$

where ϕ is the fractional porosity, ρ_{solid} is the average grain density, ρ_{H2O} is the density of water or ice, ρ_{rock} is the density of the rock, and Cp_{solid} and Cp_{H2O} are the mean specific heat capacity of the mineral grains and the specific heat capacity of the water or ice, respectively.

However, Buntebarth and Schopper (1998) have suggested recently that heat capacities of fluids and solids in a porous rock are not additive. They determined the total heat capacities of some water-filled rocks to be “considerably larger than the sum of the heat capacities of liquid and rock framework alone.” If their contention is correct, Equation (13) will have to be modified.

Where two or more fluid phases coexist, each contributes to the thermal capacity in proportion to its saturation of the pore space (Gambill, 1957; Kobranova, 1989; Somerton, 1992). In a more general

form, then, the specific heat capacity for a rock containing oil, gas, and water is given by

$$Cp_{rock} = [\rho_{solid} * Cp_{solid} * (1 - \phi) + \rho_{H2O} * Cp_{H2O} * \phi * Sw + \rho_{oil} * Cp_{oil} * \phi * So + \rho_{gas} * Cp_{gas} * \phi * Sg] / \rho_{rock} \quad (14)$$

where Sw , So , and Sg are the water, oil, and gas saturations, respectively. Somerton (1992) states that the contribution from gas can be ignored without loss of accuracy, but it is easy to include that of gas if desired.

EXAMPLE APPLICATIONS

Consider a reservoir rock with a porosity of 18% that contains oil, gas, and water, and assume an average grain density of 2.68 g/cm³, a water density of 1.03 g/cm³, an oil density of 0.9 g/cm³ (all at 20°C), and a gas density of 0.12 g/cm³ at subsurface conditions. Further assume that the subsurface temperature is 120°C at a depth of 3000 m, and that the reservoir is at hydrostatic pressure. Because porosity = 18%, $\phi = 0.18$ and $(1 - \phi) = 0.82$, also assume that the water, oil, and gas saturations in the reservoir are equal ($Sw = So = Sg = 0.333$).

Using Equation (2) in Waples and Waples (2004), which estimates thermal capacity of solid materials as a function of density, we estimate the thermal capacity of the solid material ($\rho_{solid} * Cp_{solid}$) at 20°C to be 2.19 J/cm³/K. Dividing by the grain density yields a specific heat capacity for the mineral matter of 816 J/kg/K at 20°C. Using Equation (13) from Waples and Waples (2004), we then calculate its specific heat capacity at 120°C to be 922 J/kg/K.

The density of water at 120°C is calculated from Equation (4) to be 0.978 g/cm³. Using Equations (4) and (10), the density of oil at 120°C is determined to be 0.841 g/cm³. The density of the minerals is assumed not to vary with such a small change in temperature. The density of the whole rock, which is the weighted average of the densities of the solids and fluids present, thus is calculated to be 2.31 g/cm³.

The specific heat capacity of water at 120°C is calculated from Equation (3) to be 4113 J/kg/K. The specific heat capacity of oil at 120°C calculated using Equation (7) is 2280 J/kg/K. Finally, the specific heat capacity of gas at a depth of 3000 m can be calculated from Figure 5 to be about 3350 J/kg/K.

We now can substitute these values into Equation (14). The results are given in Table 3 (Example A1). The thermal capacity of the solid material contributes

Table 3. Comparisons of Effects of Temperature (A1 and A2), Porosity (B1 and B2), Porefluid Type (C1–C3), and ice Versus Water (D1 and D2) on Thermal Capacity and Specific Heat Capacity of Porous Rocks. Shaded Blocks Show Variables that were Deferred in Each Comparison.

	Temperature		Compaction		Pore-fluid type			Permafrost	
	A1	A2	B1	B2	C1	C2	C3	D1	D2
Porosity (%)	18	18	30	5	20	20	20	40	40
Temperature (°C)	120	20	120	120	120	120	120	25	–5
Sw (%)	0.333	0.333	1	1	1	0.3	0.3	1	1
So (%)	0.333	0.333	0	0	0	0.7	0	0	0
Sg (%)	0.333	0.333	0	0	0	0	0.7	0	0
Rock density (g/cm ³)	2.31	2.32	2.17	2.59	2.34	2.32	2.22	2.02	2.01
Gas density (g/cm ³)	0.12	0.12	—	—	—	—	0.11	—	—
Thermal capacity – matrix (J/cm ³ /°K)	2.021	1.793	1.725	2.341	1.971	1.971	1.971	1.321	1.265
Thermal capacity – water (J/cm ³ /°K)	0.241	0.252	1.207	0.201	0.805	0.241	0.241	1.680	1.234
Thermal capacity – oil (J/cm ³ /°K)	0.115	0.100	0.000	0.000	0.000	0.268	0.000	0.000	0.000
Thermal capacity – gas (J/cm ³ /°K)	0.024	0.015	0.000	0.000	0.000	0.000	0.052	0.000	0.000
Thermal capacity – rock (J/cm ³ /°K)	2.40	2.16	2.93	2.54	2.78	2.48	2.26	3.00	2.50
Specific heat capacity – rock (J/kg/°K)	1038	930	1351	980	1187	1069	1021	1486	1242

2.026 J/cm³/K to the total thermal capacity. The water contributes 0.241 J/cm³/K, whereas those of the oil and gas are 0.115 J/cm³/K and 0.024 J/cm³/K, respectively. The total thermal capacity is the sum of those contributions: 2.41 J/cm³/K. Dividing by the density of the whole rock, we obtain a specific heat capacity of 1040 J/kg/K at reservoir conditions.

The thermal capacity of the water in this example is about twice that of oil and ten times that of the gas. The gas contributes only 1% of the total thermal capacity, and thus could be neglected. Even if the gas in this example were dense, it only would have contribute about 5% of the total thermal capacity. However, if gas saturation is high and the gas is not highly compressed, the replacement of water by gas could result in a lowering of the total thermal capacity (and specific heat capacity) of the rock by somewhere between 5% and 10%. Shallow, less-dense gas would reduce the thermal capacity more than deeper, denser gas.

Table 3 compares the effect of four variables (temperature, degree of compaction, pore-fluid type, and permafrost vs. water) on both thermal capacity and specific heat capacity. In each instance the lithology is assumed to be the same as that in the previous example. The differences within each comparison group are highlighted.

Under “Temperature” we see that as the temperature rises from 20°C to 120°C for the same rock ($\phi = 18\%$ in both situations), the thermal capacity and specific heat capacity both increase by 11 to 12%. The increase is the result almost entirely to the increase in thermal capacity of the mineral grains.

The “Compaction” comparison shows that as the rock decreases in porosity from 30% to 5% (both at 120°C), the specific heat capacity decreases by 27%, but the thermal capacity only decreases by 13%. The loss of water during compaction lowers both values, but the lowering of the thermal capacity is compensated partly by a compaction-induced increase in rock density of 19%.

Thermal capacity and specific heat capacity are both highest when the pore fluid is water, and lowest when the water is replaced by gas. An oil-water system is intermediate in thermal properties. In replacing 70% of the water with gas, the thermal capacity is lowered by 18%, whereas the specific heat capacity decreases by 14%.

Finally, in high-porosity sediments there is considerable difference between rocks containing permafrost and those containing water. The “Permafrost” columns compare a shallowly buried sediment ($\phi = 40\%$) in a cold region ($T = -5^\circ\text{C}$) with the same sediment in a warm region ($T = 25^\circ\text{C}$). The thermal capacity and specific heat capacities of the permafrost-bearing sediment are both 16% to 17% lower than those of the sediment filled with water.

In summary, calculation of the thermal capacity and specific heat capacity of sediments filled with a mixture of pore fluids is straightforward. Results of sample calculations show that compaction, temperature, and pore-fluid type all can result in moderate variations in both thermal properties. In the examples cited, for the same lithology under different conditions specific heat capacity varied from 930 J/kg/K to

1486 J/kg/K, whereas thermal capacities varied from 2.16 J/cm³/K to 3.00 J/cm³/K.

CONCLUSIONS

The pore fluids that occur in geological environments exhibit a range of specific heat capacities. That of water is highest, whereas those of ice (permafrost), gas hydrates, and oil are lowest. Natural gas, exemplified by methane, is intermediate between those extremes. Specific heat capacities of oil, ice, and gas hydrate are similar to or slightly lower than those of most rock minerals, whereas that of methane is high, and that of water is higher. Therefore, the higher the porosity, the higher the specific heat capacity of the porous, fluid-saturated rock.

Specific heat capacities of pore fluids, similar to those of minerals, increase with increasing temperature. The increase in heat capacity of gas with increasing temperature is opposed by a pressure-induced decrease in heat capacity. As a result, heat capacities of gases increase more slowly than those of liquids or solids.

The increase in specific heat capacity with increasing temperature can be predicted accurately for water, ice, and gas hydrates, and slightly less confidently for hydrocarbons. The variation in heat capacity of methane with pressure also can be predicted with good accuracy. Alternatively, a generalized pressure dependence can be included by assuming the fluids are at hydrostatic pressure. Even if the fluids are not at hydrostatic pressure, the actual fluid pressure would not differ from normal (hydrostatic) pressure by more than a factor of two. Therefore, it is not necessary for basin-modeling purposes to include pressure effects explicitly.

Variations in pore-fluid type can result in differences as large as about 10% in specific heat capacities of porous rocks. Existing modeling programs normally assume that water is the only pore fluid. This assumption can introduce errors in heat capacities of porous rocks and in calculated temperature profiles.

However, because water is by far the dominant pore fluid in most basins, errors introduced by neglecting thermal properties of hydrocarbons are small. Basin model developers can include the data and equations provided in this paper to improve their software.

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